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INKS

THEIR COMPOSITION AND MANUFACTURE

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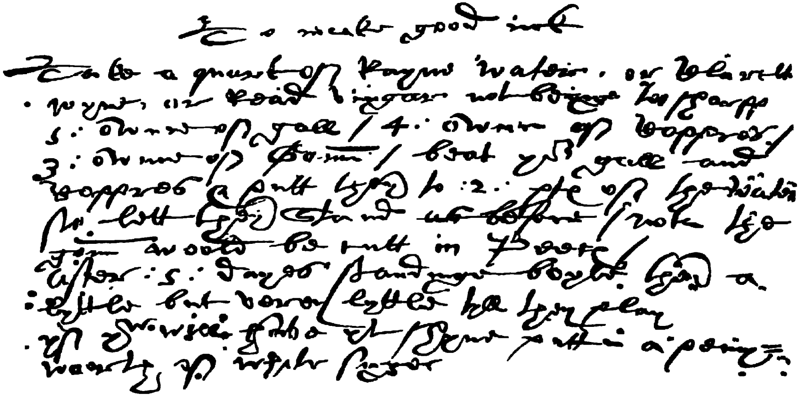

Frontispiece

INKS

THEIR COMPOSITION AND MANUFACTURE

INCLUDING METHODS OF EXAMINATION AND
A FULL LIST OF ENGLISH PATENTS

BY

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AND
T. C. HEPWORTH

WITH 46 ILLUSTRATIONS, INCLUDING 4 PLATES

LONDON
CHARLES GRIFFIN & COMPANY, LTD.
EXETER STREET, STRAND
1904

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Printed by BALLANTYNE, HANSON & Co
London & Edinburgh

PREFACE

SOME three years ago we were engaged in a scientific inquiry as to the composition of certain fluids used as writing ink. As this work led us beyond the limits anticipated, and to the making of many experiments not actually required at the time, and as there is need for a volume dealing adequately with the subject, we thought it advisable to embody the results in book form. We found, it is true, a few small books on ink and many allusions to ink-making in old volumes and isolated papers in scientific journals; but it seemed to us that the matter required more comprehensive treatment, and the present work may be regarded as an attempt to supply that want.

As far as time permitted we have tested the various formulæ quoted, but, as may be seen by reference to the patent list at the end of the book, there are so many cases of slight variations in composition that we have often contented ourselves with a record of the statements put forward.

We have pleasure in tendering our best thanks to those who have assisted us in our work.

To Mr. *R. M. Prideaux*, in particular, we are indebted for the excellent drawings of the various galls (pp. 37–46), the details of which could not have been nearly so well shown by photography.

Messrs. *Newman and Co.*, of Soho Square, were good enough to afford us much information with regard to sepia preparations, and to supply us with dried specimens, &c., for analysis.

The photographs of fossil cephalopoda were taken by us at the Geological Museum, Jermyn Street, by the courtesy of the Curator.

To the authorities at Kew we are indebted for permission to photograph in the Museum and in the Herbarium.

The *Badische Company* kindly supplied us with specimens of aniline dye-stuffs and much valuable information regarding them.

We have also to thank Messrs. *Keller and Co.*, who have kindly allowed us to use certain blocks illustrative of printing-ink machinery, and have sent us samples of various permanent colours.

Lastly, our thanks are due to Messrs. *Madderton and Co.*, of Loughton, for specimens of permanent preparations made by them.

C. A. M.
T. C. H.

GRAY'S INN, LONDON W.C.
August 1904.

LIST OF ENGLISH PATENTS.

WRITING AND COPYING INKS.

Date.	No	Name	Subject-matter
1688	258	Holman.	Powder for black ink. To be mixed with water, beer, &c.
1764	809	Cummings	Composition for writing on skins, paper, &c
1768	906	Dring.	Making ink into a cake or solid.
1780	1244	Watt	Copying presses and ink.
1809	3214	Folsch and Howard.	Permanent writing ink.
1825	5285	Giroud	Ink from chestnut wood ("damaja-vag").
1837	7313	Stevenson.	Indelible safety paper (impregnated with $MnCl_2$ and $K_4Fe(CN)_6$).
1837	7341	Aldrich.	Colours rendered applicable to writing.
1837	7342	Stephens and Nash.	Indelible ink Carbon in solution of resinous soap.
1837	7474	Whitfield.	Indelible ink. Lamp-black in linseed oil, &c.
1839	8175	Normandy.	Writing inks.
1840	8770	Scott.	Indelible ink. Gas-black, indigo and Prussian blue in gall and logwood ink.
1843	9667	Roberts	Composition of ink.
1844	10,329	Mackenzie	Writing fluids.
1846	11,474	Reade.	Indelible ink. Soluble Prussian blue in gall ink. Also red ink, marking inks, and printing inks.
1855	970	Dépierre.	Ink from decoction of alder flowers and iron salt.
1855	16[illegible]6	Wood.	Lake of alum and cochineal dissolved in ammonia solution.
1856	342	C. and G. Swann.	Writing and copying ink. Chrome logwood ink.
1857	1112	Underwood.	Copying paper. Writing with logwood decoction, and moistening with K_2CrO_4 solution before copying.

Date.	No.	Name.	Subject-matter.
1858	1132	Henry.	Copying ink. Addition of glycerin.
1858	1900	Winstone.	Copying ink. Addition of glycerin. (*Prov.*)
1859	801	Ballande.	Safety paper. Paper impregnated with metallic salt. Ink a solution acting upon the salt.
1859	1744	Scoffern.	Ink. A solution of animal or vegetable fibre in "copperised" ammonia.
1860	388	Ballande.	Safety ink and paper. On lines of pat. of 1859.
1860	531	Melville.	Indelible ink. Plumbago with resin, gum, &c., alum, and a suitable colouring-matter.
1861	2072	Stevens (Cross).	Indelible anti-corrosive ink. Aniline dyes used with carbon.
1862	675	Clark (Armand).	Inks from aniline dyes.
1862	1213	Roberts.	Copying ink. Use of glycerin, molasses, and extract of *abelmosch* seeds.
1862	2235	De la Rue.	Writing inks from aniline waste, &c.
1863	1418	Friederich.	Ink from logwood and potassium bichromate and ferrocyanide.
1863	1810	Godel.	Alkaline tannate or logwood solution treated with metallic iron. (*Prov.*)
1864	2223	Baildon.	Safety ink and paper. Colour of paper changed by acid in the ink.
1864	2506	Newton.	Method of oxidising ink. (*Prov.*)
1865	536	Newton.	Do. do. do.
1865	2207	Ellis.	Indelible inks. Colouring-matters precipitated by silicic acid and dissolved in a soluble silicate solution.
1867	106	Cooley.	Ink powders. Prepared by extracts of dye-stuffs with metallic salts, &c.
1868	2103	Cooke.	Copying ink. Addition of glycerin. (*Prov.*)
1869	47	Cooke.	Copying ink. As in the patent of 1868.
1870	1803	Pinkney.	Ink from aniline salts with oxidising agent and metallic salt, of which nickel is specially claimed.
1871	2745	Pinkney.	Ink from aniline salt, oxidising agent, and uranium or vanadium salt.
1873	258	Ottensohn.	Ink from tin waste.
1873	262	Halfpenny.	Incombustible ink and paper. Addition of asbestos to paper. Plumbago ink.
1873	1082	Carter.	Oxidising gall ink by air current.
1873	3814	Tessonnières.	Prevention of deposits in ink by addition of oxalic acid or oxalate.

Date.	No.	Name.	Subject-matter
1873	3684	Hyatt	Incombustible paper and ink. Addition of asbestos.
1874	1078	de Zuccato.	"Papyrographic" copying ink. Paper coated with varnish. Ink, a solution of caustic alkali with colouring matter.
1874	1830	Gaffard.	Indelible ink. Carbon in solution of alkali silicate.
1874	2009	Casthelaz	Ink obtained by oxidising H_2SO_4 solution of aniline.
1874	2039	Mitscherlich.	Tannin for ink extracted by heating the substance containing it with sulphurous acid under pressure.
1874	3150	de Zuccato.	Improvements in Patent No. 1078 of 1874.
1874	4080	Petit.	Copying-ink pencil. Aniline dye with plumbago and adhesive material. (*Prov.*)
1874	4421	Knab	Black for ink obtained by heating gas-tar with lime in a retort
1875	1620	Grawitz.	Manufacture of aniline black.
1875	4484	Joly.	Ink prepared by action of tungstic acid on colouring-matters (*e.g.*, of logwood, elderberry, &c.)
1876	974	Byford.	Dry copying ink powder.
1876	4820	Plateau.	Portable ink. Absorbent material saturated with aniline dye, &c
1877	2380	Kromer.	Sympathetic ink. Dry tannin and anhydrous ferrous sulphate made into paste with benzene and varnish.
1878	1580	Jacobsohn.	Copying ink powder. Solution of aniline dye, sugar, gum, &c., evaporated to dryness.
1878	2636	Richmond.	Indelible ink, containing aniline black, and also the substance for forming aniline black.
1878	4606	Kwaysser and Hasak	Copying ink. Aniline colour in alcohol and water.
1878	5122	Hickisson.	Ink from vanadium or its salts with oxidising agent to form a mordant (pref. salt of nickel or copper)
1879	526	Fargue.	Ink attached to cavity of pen by adhesive material.
1879	2256	Rosefeld	Copying apparatus (gelatin) and aniline ink
1879	3391	Jefferies.	Aniline inks.
1879	3499	Taylor.	Formation of aniline black [also as marking ink]. (*Prov.*)
1879	4187	Harm.	Aniline and metallic inks for copying apparatus

Date	No.	Name.	Subject-matter.
1880	2606	Bergel.	Marking fluid for paper silhouettes [KNO$_3$ solution] (*Prov.*)
1881	741	Stoddart.	Manufacture of ink from spent tan liquors.
1881	903	Grunwald.	Dry copying ink. [Uranium acetate, sugar, glycerin with logwood extract and alum, or aniline colour]. (*Prov.*)
1881	1002	Priestman and Longshaw.	Ink from waste tan liquor and iron salts. (*Prov.*)
1881	2948	Schmitt.	Copying apparatus. Gelatin with glycerin and chrome alum. Ink which contains uranium salt and colour (*e.g.*, indigo), acts chemically on substance in the jelly.
1881	3410	Mothe.	Fireproof ink. Writing or printing with ink containing platinum chloride on paper containing asbestos.
1881	3905	Gurney.	Ink from spent tan liquor and iron filings.
1881	3957	Sachs.	Sensitive ink for tracing designs. Action of light on bichromate.
1882	728	Reissig.	Indelible ink. Printing ink incorporated with ferrous and ferric salts, and thinned with turpentine, &c. (*Prov.*)
1882	3583	Detmold.	Aniline or gall inks, containing alcohol, spirit of camphor, &c. Drying instantly on contact with the paper.
1883	859	Fonseca & Co.	Indelible ink. Logwood extract, sugar, aniline black and soot.
1883	3008	Bolton.	Non-smearing copying ink. Addition of ginger and gum arabic to iron gall ink. (*Prov.*)
1884	7160	Friend.	Papyrographic ink. Iron, tannic acid and glycerin.
1885	440	Armour.	Ink removable by washing.
1885	8241	Frisher.	Ink from waste logwood, and potassium bichromate of dyeing vats.
1885	9240	Wass.	Indelible ink from carbonised sugar scum.
1886	3179	Payne.	Ink tablet for inking rubber stamps.
1887	730	Hunly.	Sympathetic ink. Magnesium platinocyanide.
1887	15079	Hackney.	Addition of CaCl$_2$ to ink to prevent drying. Blotting paper containing sodium sulphate or borate to decompose the CaCl$_2$ so that the writing can dry.
1887	12925	Groth.	Indelible ink. Black compound from aniline in suitable medium.

Date.	No.	Name.	Subject-matter.
1888	645	Dimitry.	Solution of aniline colour with gelatin and potassium bichromate. Exposed to sun.
1888	7149	Smith.	Manifold copying ink (aniline in water, HCl and alcohol), used with slab of china clay, starch, glycerin, and water.
1888	7472	Quelch.	Invisible ink. Writing with solution of KNO_3 or KCl on non-glazed surface, and applying hot wire.
1889	2360	Brasier and Knowles.	Writing ink composed of alkaline extract of fibrous plant, *Bauhinia Vahlii*.
1889	8971	Mills.	Sanitary ink. Addition of an antiseptic agent.
1889	14,288	Ashton.	Dry inks. Soluble colours with gum, &c., dried on wood, shavings, &c.
1889	15,565	Pulford.	Invisible ink for envelopes. Uranium acetate and potassium ferrocyanide with white lead applied with lithographic varnish. Steam brings about reaction.
1890	2011	Conrad and Lilley.	Copying ink. Addition of indigo carmine and aniline black with glycerin and magnesium chloride to an iron gall ink.
1890	2130	Tscholen.	Invisible ink. Writing on smooth surface with chalk water and dusting letters with powder, *e.g.*, graphite.
1890	10,401	Conrad	Copying ink. Addition of deliquescent salts (*e.g.*, ammonium nitrate), and glycerin.
1890	10,905	Piffard.	Copying paper. Paper treated with gallic acid—iron ink. No press required.
1890	15,857	Higgins.	Ink for stamps. Oleic acid and dyestuff, *e.g.*, methyl violet.
1890	15,858	Higgins.	Idem. Solution of aniline colour in essential oil.
1890	16,757	Just, Weiler, and Heidepriem	Safety ink. Carbon black, vanadium compounds, galls, &c.
1890	1[illegible]373	Beales.	Copying ink and prepared paper. No damping paper required.
1891	1616	Leech and Harrobin.	Indelible ink. Turpentine, asphalt, resin, alum, beeswax and colour.
1891	3247	Coën.	Copying ink. Glycerin and candied sugar in ordinary ink.
1891	5437	Sherwood.	Copying ink. Soluble aniline dye, borax, water, and boiled linseed oil.

Date	No	Name	Subject-matter
1892	93	Higgins	Stamping ink. Aniline colour with fixed oil and carbolic acid.
1892	18,721	Friswell and Leeds.	Copying ink. Lamp-black in solution of aniline dye evaporated, and residue mixed with lithographic varnish.
1893	7263	Blancan	Indelible ink. Aluminium powder with protective varnish.
1893	16,830	Hollyer	Sanitary ink. Addition of juice of lesser celandine.
1894	3230	Neustaedt and Goldmark.	Dried ink. Granules of non-porous substance covered with dried ink.
1894	5078	Neustaedt and Goldmark.	Dried ink. Glass or metal, &c., coated with pigment and binding material.
1895	6038	Thacker	Safety paper. Coated with colour. Ink removes the colour of portion written on.
1896	3450	Adams	Sympathetic ink. Dilute H_2SO_4 (1 : 17), writing made visible by heat.
1896	17,226	Temple	Non-staining ink. Addition of saline compound, *e.g.*, ordinary salt.
1897	21,830	Spencer.	Dried ink. Aniline dye with sodium bicarbonate and acid to produce effervescence and diffuse colour in water.
1897	21,991	Möller	Invisible and indelible ink. Alum and white garlic juice visible on heating.
1898	5294	Izambard	Use of Rontgen rays in writing.
1898	24,644	Lichtentag.	Indelible ink. Carbon in soap and water or other medium.
1899	6727	Kretschmann	Sympathetic ink. Paper treated with solution of cobalt chloride. Ink a solution of rock salt.
1899	8976	Bachem.	Sympathetic ink. Two substances, *e.g.* cobalt chloride and magnesium platino-cyanide, one becoming visible and other disappearing on heating.
1899	14,057	Power.	Rapidly-drying ink. Tincture hamamelis, tincture of iron, and gum arabic in spirits of wine.
			Red ink from rose petals.
1900	1296	Izambard.	Copying by means of Rontgen rays.
1900	7367	Kretschmann.	Sympathetic ink. Paper treated with non-hygroscopic cobalt salt. Writing with solution of salt and substance (*e.g.*, vinegar) to produce hygroscopic salt.

Date.	No	Name	Subject-matter
1900	3807	Brown	Copying paper. Paper treated on one side with hardened gelatin, and on the other with deliquescent substance (*e.g.*, $CaCl_2$), and solution of substance not affected by writing ink. No damping required.

MARKING INKS.

1848	11,474	Reade.	Ammoniacal solution of silver tartrate. Addition of gold salts.
1856	738	Bulton	Platinum salt (Pt_2Cl_6), added to the silver. (*Prov.*)
1858	2316	Dunn.	Marking ink pencils. Silver salts with black lead or other provisional colouring-matter.
1864	1828	Möller.	Red ink-madder with cochineal, magenta or carmine. Alum as mordant. (*Prov.*)
1864	2511	Moller	Madder extract with alkali salt in alcohol, gum and vermilion. Alum used previously as mordant.
1877	379	Schroll.	Marking ink pencil. Composition of clay, silver nitrate, or other soluble silver salt and plumbago.
1878	5122	Hickisson.	Vanadium salts, with oxidising salt as mordant. For solid pencil, gum, dextrin, clay, &c., added
1879	3499	Taylor.	Formation of aniline black within the fabric.
1880	1771	Johnson.	Impregnating fibres with mixture containing ortho-nitro-phenyl-propiolic acid, reducing agent and alkali, and developing with heat.
1880	1838	Sachs.	Formation of dye-stuffs from polysulphides of heavy metals.
1881	460	Johnson.	Use of sulphides or sulpho-compounds of alkali metals as reducing agents in previous patent
1882	5046	Langbeck.	Coloured marking inks. Salicylic acid, turpentine oil, spirits of wine, glycerin, and colouring-matter (vermilion, &c.).
1883	751	Hickisson and Langbeck.	Colour mixed with solution of caoutchouc in carbon bisulphide.

Date	No.	Name.	Subject-matter.
1883	752	Hickisson and Langbeck.	Colour mixed with bases of arsenic pentoxide, turpentine, and glycerin. Pencils from same mixture.
1884	9149	Hickisson.	Pencil with marking point ($AgNO_3$ with KNO_3) at one end and mordant (pyrogallol, wax and borax) at the other.
1884	15,961	Hickisson.	Mordant for pencil. Moistened and applied to linen.
1885	3980	Simpson.	Mordants rendering ordinary writing insoluble in water.
1888	647	Domitry.	Soluble colour with gelatin and potassium bichromate, writing exposed to sunlight.
1893	5316	Hickisson	Aniline dyes soluble in oil dissolved in *e.g.*, castor oil, and solutions thinned with turpentine. For pencils, mixed with suitable base.

PRINTING INKS.

1772	1012	Rowley.	Ink for printing playing cards in colours.
1821	4601	Martin and Gratton.	Soot of burnt coal-tar as pigment.
1831	6182	Smith and Doher.	Delible ink for copying books.
1835	6906	Bird.	Printing ink. Use of a mineral earth as pigment.
1853	483	Goodell.	Use of residue from purification of rosin oil.
1853	1900	Gwynne.	Powdered coal as pigment.
1853	1920	Newton	Use of residue from distillation of rosin oil.
1853	2243	Maumene	Carbonised lignite as pigment.
1854	1575	Archer.	Paper carbonised with sulphuric acid as pigment.
1854	2490	De la Rue.	Addition of glycerin.
1855	32	Livesay.	Ordinary typographic ink mixed with varnish, rosin, and Venice turpentine.
1855	320	Kuhlmann.	Addition of silicates to letterpress ink.
1855	1918	De la Rue.	Addition of manganese borate.
1856	400	Grant.	Addition of odoriferous essential oils.
1856	516	Brooman.	Pigment from bituminous shale and

Date.	No.	Name.	Subject-matter.
1856	2406	Underwood and Burt.	Copying printing ink. (Gall and ferrous sulphate.)
1857	1112	Underwood.	Copying printing ink. (Logwood extract.)
1857	1518	Matthews.	Green ink. Chromium oxide and varnish.
1857	1744	Seropyan.	Ink for cheques.
1858	1187	Stuart.	Residue from distillation of bituminous substances as pigment.
1859	130	Viette.	Lithographic ink containing gutta-percha.
1859	348	Moss.	Ink for cheques.
1859	1282	Hadfield.	Apparatus for varnish manufacture.
1859	2081	Collins.	Transfer ink.
1859	2399	Palmer.	Aniline by-product as pigment.
1860	388	Ballande.	Safety printing ink.
1860	1445	Therry.	Pigment prepared from carbonised schist.
1860	2640	Neal.	Grinding mills.
1862	767	Brooman.	Inks for printing on glass.
1862	2654	Prince.	Use of petroleum products in lithographic varnish.
1862	3074	Croc.	Telegraph ink. Aniline in dilute alcohol, thickened with gluten.
1863	1564	McLean.	Pigment from shale. (*Prov.*)
1863	3204	Hughes.	Ink for cheques. Compound of stannic acid and chromium oxide.
1864	2854	Rowley.	Use of pitchy substance from distillation of cotton oil.
1865	3325	Newton.	Oil substitute prepared from glue or gelatin.
1866	367	Holmes.	Animal pitch (bone oil pitch) as lampblack substitute. (*Prov.*)
1866	1737	Holmes.	*Idem.*
1868	2578	P. and W. Hodge.	Pigments. Oxides of iron heated with carbonised peat.
1869	439	Binko.	Indigo printing ink.
1869	2890	Kirchner and Ebner.	Delible printing ink. Ferric hydroxide with tannin in a varnish.
1869	2946	May.	Non-oleaginous inks. Glycerin, gums, and pigment.
1869	2993	Kloen.	Water-colour inks. Pigments with glycerin, gums, sugar or other substances soluble in water.
1869	3543	Edwards.	Photo-mechanical ink. Extra greasy ink.
1870	967	Jackson.	Grinding mills.
1870	1419	Lawrence.	Ink containing glycerin, gum, sugar, and pigment.

Date	No.	Name.	Subject-matter
1870	1803	Pinkney.	Use of aniline salts with nickel salts and an oxidising agent.
1870	2762	Lake (Toppan).	Use of petroleum products.
1871	680	Lake.	Copying ink. Use of pigment soluble in water and of soluble gums.
1871	2745	Pinkney.	Use of aniline salt with salts of vanadium and nickel.
1871	3305	McCready.	Apparatus for blending colours.
1873	2133	Little.	Telegraphic apparatus. Ink of aniline blue in glycerin.
1873	3129	Mackay.	Use of oil recovered from waste fabrics.
1873	3176	Newton	Pigment for printing fabrics.
1873	3508	Kingdon	Grinding mills.
1873	3084	Hyatt.	Fireproof ink. Addition of asbestos powder.
1873	3800	Smith and Fountain.	Heating printing ink to uniform temperature before use.
1873	4100	Thomas	Use of heavy oils and pitches from tar.
1874	268	Clark	Apparatus for manufacture of lamp-black.
1874	1078	de Zuccato	Papyrographic ink. Caustic alkali solution and vandyke brown.
1874	1839	Tongue	Carbon in a silicate solution as indelible ink.
1874	1975	Clark	Stamping ink. Solution of colour in alcohol and glycerin.
1874	4421	Knab	Manufacture of pigment from gas tar &c.
1875	605	Whitburn.	Ink for printing on wood.
1875	1020	Clark	Production of aniline black for printing.
1875	1921	Holyoake	Transfer ink. (*Prov.*)
1875	3762	Edison.	Ink for autographic printing. Printers' ink thinned with castor oil.
1876	1602	Henet.	Printing on glass.
1876	2268	Brooks	Coloured printing inks. Special varnish.
1876	2021	Zingler.	Metallic printing inks. Solution of albumen as vehicle.
1876	3270	Tongue.	Pigments from anthracite and other coal. (*Prov.*)
1876	4470	Pinkney.	Ink for cheques. Use of ferrocyanides with aniline or vegetable colours.
1877	160	Tongue	Pigments from anthracite, &c. (*Prov.*)
1877	895	Pumphrey	Autographic ink. Aniline colours in acetic acid and glycerin.
1877	956	William.	Boiling oil. Use of steam.

Date.	No	Name	Subject-matter.
1877	[illegible]	Howard.	Pigment from peat charcoal.
1877	3407	L'Heureux and Lagny.	Engraving ink containing sugar, gum arabic, and silicates.
1878	2706	Liston.	Ink for printing on earthenware. Pigment with glycerin or molasses.
1878	5098	Winterholf.	Ink for china, wood, iron, &c. Pigment with varnish of oil, resins, Venice turpentine, wax, suet and flux.
1879	141	Haddan	Metallic powder incorporated with solution of silicate.
1879	402	Cammack and Argall.	Kaolin clay as a base for the pigment.
1879	2518	Gray.	Preparation of varnish by treating oil with hot air.
1879	3391	Jefferies	Transfer ink. Treacle and glue
1879	4204	Nesbit	Ink for cheques. Aniline printing ink.
1879	4524	Gestener.	Water colour transfer ink. Mixture of a water colour pigment in aniline with glycerin, varnish, syrup and mineral pigment. (*Prov.*)
1879	4645	Kesseler.	Ink for zincography. Pitch, tar oil, fatty acid, aniline violet and residue from distillation of rosin oil
1879	4788	Imray.	Transfer printing inks.
1879	4997	Haddan.	Ink for cheques. Bichromate, ferrous sulphate, ferrocyanides, logwood, oxalic acid and glycerin. (*Prov.*)
1879	5232	Wirth.	Coal tar as pigment. (*Prov.*)
1880	827	Pfleiderer.	Ink for glass. Pigments with copaiba balsam, Venice turpentine, rosin oil and driers.
1880	1028	Klein.	Ink for printing oil cloth
1880	1615	Alexander.	Pigment from bitumens and hydrocarbons. (*Prov.*)
1880	1838	Sachs.	Use of dyeing substance in printing ink.
1880	1971	Savigny and Collineau.	Use of a special vegetable colouring-matter.
1880	2216	Kesseler.	Ink from pitch, fatty acid, aniline violet, and tar oil.
1880	3418	Ungerer.	Colouring composition for impression rollers. (*Prov.*)
1880	4591	Bertram.	Flexible ink. Aniline, acetic acid, glucose, glue, glycerin and water.
1880	4693	Bartard.	Use of oil from cotton waste.
1880	4840	Watt.	Ink for calico printing.
1880	4874	Boult	Ink for celluloid. Aniline colours in carbolic acid.
1881	375	Dupré and Hehner.	Ink for cheques.

Date.	No	Name.	Subject-matter.
1881	436	Poirson.	Transfer ink for leather, &c. Containing salts melting in their water of crystallisation, *e.g.*, alum or sodium sulphate.
1881	814	Marie and Bonneville.	Use of nitric esters of sugars. (*Pro.*)
1881	903	Gard and Cobley.	Use of tannin black from leather waste as lamp-black substitute.
1881	1002	Longshaw and Priestman	Tannin black from spent tan liquors (*Pro.*)
1881	1203	Brackelbusch	Printer's varnish without linseed oil. Colophony and paraffin oil. (*Pro*
1881	2103	Bastand.	Use of oil extracted from engine cotton waste.
1881	2274	W. G. and R. R. White	Polychromatic printing ink containing aniline dye-stuffs, &c.
1881	2868	Jensen.	Ink from pitch, anthracene oil, tar oil, aniline colour, and lubricating soap. (*Void.*)
1881	3410	Methe.	Fireproof printing ink. Use of asbestos powder
1881	3605	Gurney	Tannin black from waste tan liquors.
1881	3657	Sachs.	Ink for impressions of patterns. Chromium compound, &c.
1881	3762	Clark	Autographic transfer ink. Contains proteids, bichromates, ferrocyanides and alums.
1882	728	Reissig.	Indelible printing ink. Linseed oil varnish, lamp-black, and ferric chloride. (*Pro.*)
1882	3086	Wirth.	Manganese peroxide as pigment.
1882	3248	Gibson.	Metallic inks. Metallic powder mixed with naphtha and solution of rubber in carbon bisulphide.
1882	4106	Claus.	Iron sulphide incorporated with rosin, gum, or fused sulphur.
1883	949	Nesbit.	Ink for cheques. Use of decoction of alkanet root.
1883	3638	Lake.	Ink for india-rubber goods. Caoutchouc, naphtha, red lead, and sulphur.
1884	2268	Baseley.	Grinding mills.
1885	9249	Wass.	Pigment from sugar scum
1885	9413	Macrone.	Varnish from seed oil, rosin, paraffin wax, bees-wax, and copal varnish.
1886	606	Rousset.	Varnish for fixing transfers. Mineral pitch, heavy benzine, and copaiba essence.

Date.	No.	Name	Subject-matter.
1886	1601	Gutheil.	Lithographic ink of intense colour. Venetian soap, wax, mastic, shellac, Venice turpentine, lamp-black or soot rubbed with water for use.
1887	1076	Schlumberger.	Addition of vegetable colouring-matter (alizarine) altering colour on addition of alkali. (*Opposed and not granted.*)
1887	17,925	Groth.	Antiseptic ink. Aniline black in aniline, carbolic acid, &c.
1888	3321	Bensinger.	Ink for celluloid. Aniline dye-stuff in carbolic or acetic acids.
1888	13,968	Neilson, Harrap and Brown.	Antiseptic ink. Use of permanganate or pigments used in sanitary wall-paper.
1888	15,457	Jones.	Invisible printing ink. Cobalt salt in dilute alcohol. Inking rollers to be covered with absorbent material, *e.g.*, flannel.
1889	6287	Weight.	Sanitary ink. Part of paper rendered transparent with "medicating oil."
1889	8971	Mills.	Sanitary ink. Addition of antiseptic.
1889	15,839	Browne.	Use of semi-fluid bitumen (maltha) with or without black pigment.
1889	20,830	Huelser.	Use of fine coal dust as pigment.
1890	11,168	Holt.	Ink from residue from distillation of petroleum with resin, gum, and pigment
1890	15,743	Davison.	Imitation metallic printing inks. Nitrobenzene aniline product, picric acid, varnish, spirit, soap, rosin, &c.
1890	16,689	Lake.	Non-clogging ink Vaseline, fatty oil, and pigment.
1890	16,757	Just, Weiler, and Heidepriem.	Ink for cheques &c. Black from sugar, or carbon black, caustic potash, oxalic acid. Indian ink, vanadium compound, galls, gum arabic, aniline colour, and water
1891	873	Hudson and Hills.	Antiseptic ink. Permanganate or eucalyptus, &c., with glutinous compound.
1891	12,104	Brandt.	Zincographic ink. Antimony black, bone black, resins, strong varnish, Berlin blue and ordinary printing ink.
1891	12,200	Bertling.	Lithographic transfer ink.
1891	17,635	Dreyfus.	Resinates of coal tar dye-stuffs used as pigments.
1892	12,280	Chamberlain.	Ink for cartridge case. Varnish, pigment, and drying oil.

Date	No.	Name	Subject-matter.
1893	7263	Blaneau	Metallic ink. Aluminium powder with protective varnish.
1893	12,863	Bibby	Use of cotton seed "foots" with other usual ingredients.
1894	6268	Degroote and Aulnois	Colour printing ink. Pigment boiled linseed oil, siccative and caoutchouc.
1894	13,070	Cardeaux	Printing from raised type on tin foil. Addition of vaseline to ink.
1894	20,423	Barnwell	Printing several colours in one impression. Inks in strips on rollers prevented from mixing by addition of castor oil, turpentine, tar oil, copaiba balsam, sulphuric ether, ammonia and ipecacuanha.
1895	955	Priestley and Swann.	Metallic inks. Bronze powder, &c., with varnish and lard or fat.
1895	6038	Thacker.	Inks for wood, canvas, paper, &c. Surface covered with coloured layer which can be removed by suitable chemicals. (Cheque ink.)
1895	17,868	Ballet	Printing ink for imitation type-writing. Aniline dye-stuff used.
1896	8376	Taylor and Cooke.	Printing in several colours in one impression. Inks prevented from mixing by addition of copaiba balsam, glycerin, sandal wood oil, petroleum turpentine, tincture of myrrh, chloroform and ammonia.
1896	12,198	Torrance	Grinding and mixing inks. Differential gearing for rotating rollers at different speeds.
1896	16,274	Sharp.	Metallic ink suitable for stencil machines. Metallic powder with gum arabic, linseed oil, rosin oil, dextrin, red lead, litharge and turpentine.
1896	18,131	Michel-Dansac and Chassagne	Coloured ink. Albumen preparations with specified coloured pigments.
1896	20,992	Webb.	Safety ink for copper and steel plate printing. Aniline colour in base of flour and magnesium oxide with sodium carbonate and soap.
1896	30,121	Boult.	Metallic ink ("*direct-or*"). Varnish and oil, rosin, &c. with bronze powder.
1897	3,799	Gentele	Cellulose or wood powder as substratum for colours.
1897	9121	Taylor	Printing in several colours simultaneously. Addition of powdered manganese and alcohol to substances enumerated in Pat. 8376 of 1896.

Date	No	Name	Subject matter.
1897	18,53.	Ogilvy.	Mixed pigments and varnish incorporated by use of superheated steam or steam under pressure, and volatile products condensed.
1897	19,763	Webb.	Fugitive safety ink. Base of dextrin and treacle with glycerin, aniline dye-stuff and antiseptic agent.
1897	23,080	Hadley and Sephton	Ink for etched designs on glass, &c. Contains wax, Canada balsam, soap, and lamp black.
1897	24,504	Stoop	Substitute for linseed oil. Use of drying mineral oils, *e.g.*, grisee oil
1897	29,728	Banner.	Substitute for linseed oil. Colophony in suitable solvent wholly or partially saponified with caustic soda or sodium silicate; or use of lime-rosin.
1897	30,104	Bunger.	Inks used in production of colour prints.
1898	5294	Izambard.	Radiographic or X-ray proof ink. Metallic or calcareous powder with boiled oil and alkali bromide
1898	11,951	Gothilfe	Printing waterproof fabrics. Metallic powder (nickel) with egg albumen or other thickening agent.
1898	20,356	Pitt.	Use of gelatinous compound from kelp.
1898	23,071	Stoop.	Use of natural drying mineral oil (grisee oil) in varnish.
1899	17,557	Printing Arts Co. and Orloff	Use of inks of different consistency in colour printing.
1900	13,145	White.	Polychromatic printing. Special sheets of composition containing the colours.
1900	14,886	Ogilvy.	Admixture of ink effected by heating and mechanical agitation. No mill used.
1900	17,126	Hofer.	Ink for printing transparencies on celluloid. Pigments and mixture of ether, camphor, paraffin oil and manganese.
1900	17,783	Stevenson.	Printing designs changing colour on exposure. Use of combination of permanent and non-permanent colours.
1900	23,231	British Oil Mills Co. and Wass.	Use of residuum from purification of cotton-seed oil.

Date.	No.	Name	Subject-matter.
1901	1366	Hoz.	Use of dyeing pigments and development and fixing of printing on the fabric.
1901	5168	Imray.	Use of iodophenolthiosulphonates as pigments.
1901	6061	Wass.	Use of solution of resin in mineral oil as varnish.
1901	8645	Tellkamp.	Autographic ink.
1901	12,826	Wechsler.	Lithographic printing. Ink for continuous working. Pigment, varnish, glycerin, alkali salt, tartar, and turpentine.
1901	23,892	Lilienfeld.	Fixing varnish for pigments for textile fabrics.
1902	8371	Schmiedel.	Production of dark shade on coloured ground. Use of a solution of a resin with or without glycerin.

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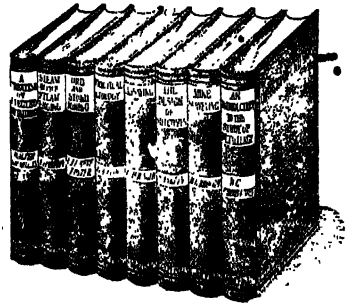

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HISTORICAL INTRODUCTION.

CONTENTS.—Ancient Egypt—Old papyri—Progress of writing—Herculaneum fragments—Carbon inks—Iron gall inks—The Lindisfarne Gospels—Transition from carbon to gall inks—Domestic ink-making—Scientific experiments—Unoxidised gall inks—Aniline inks—German regulations—Other inks.

Ancient Egypt. The earliest use of a liquid which can be described as "ink" is found in those documents on papyrus which have been among the archæological treasures of Egypt. Although the history of Egypt has been traced back for a period of more than four thousand years, and papyrus was employed as a writing material there from very remote times, the oldest specimen of the material extant is a roll which dates from B.C. 2500.[*] This possibly refers to the oldest specimen which bears decipherable characters, for Professor *Flinders Petrie* has found fragments of papyri which date from a thousand years earlier.[†] As Egypt is still the subject of exploration, and as perishable articles have been found of a still earlier period than that last mentioned, we may reasonably hope that ink-written records may some day come to light which will carry back the history of the country to a more remote time. Professor *Flinders Petrie* found in one tomb, dating from 3500 B.C., baskets, a coil of palm rope, wooden mallets, and chisels left behind by the workmen, together with some pieces of papyrus which were almost white; and he attributes the excellent condition of these things to the preservative nature of the clean dry sand in which they had been buried for so many centuries.[‡]

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[*] *British Museum Guide*, 1896, p. 312.

[†] *Journal of the Camera Club*, Nov. 18[illegible].

[‡] *Ibid.*

Old Papyri.—In Case A (Greek Papyri), British Museum, can be seen a number of specimens dating from the first century of the Christian era, and although in many cases the papyrus is merely in fragments, the ink is as black as it was the day that it was applied. The lettering in many of these papyri is extremely beautiful, and compares very favourably with much of the handwriting that some of us have to decipher to-day. And it would seem quite clear from an examination of many of these writings that the implement employed was a pen and not a brush. The papyrus in some instances is of a very light drab colour, and on this surface the old writing stands out with startling distinctness; but when the material has assumed a dark brown or yellow tint, the writing is not so distinct, although the quality of the ink is quite as good.

That papyrus was not a cheap material is shown by a specimen here, labelled "Aristotle on the Constitution of Athens. The only extant MS. of the work, brought from Egypt in 1890. Written about A.D. 100, in four rolls, in four different hands, on the back of the papyrus which had already been used [in A.D. 78–79] for the accompts of a farm-bailiff named Didymus, near Hermopolis."

Another specimen of great interest lies close to the one first mentioned, namely, fragments of the *Theogonia* of Hesiod. It is written in a firm and large hand in very black ink, and the label tells us that its date is probably the fourth or fifth century, "contemporary with the early MSS. on vellum, and so marking the transition from the one material to the other."

Progress of Writing. The various specimens shown in the King's Library at the British Museum, in Cases A—E, are designed to illustrate the progress of writing from the second century B.C. to the fifteenth century of our era, and at the same time they afford testimony as to the kind of ink employed during the period covered. The basis of the black ink used on papyrus by the ancient scribes was undoubtedly carbon, a substance which had the advantage of being easily procurable, while at the same time it was indestructible except by fire. It was probably prepared in the form of vegetable or animal charcoal, and was mixed with gum, oil, or varnish. Possibly, for the finer writing, water, with gum or glue as a binding material, was the medium mostly employed, for it would flow more readily from the reed pen or quill used by the writer.

It is certain that the art of writing has a remote antiquity, and that the power of recording thoughts in this way marks a distinct line of demarcation between civilised man and the savage. It is a matter of interest to consider the many different materials which have been used for writing upon in early times besides papyrus. Soft wood cut into slices and planed and polished was used in various countries, the pen being a metal stylus, which simply scratched or indented the material. Later on, the wood tablet with a thin coating of wax was employed, and the writing upon it in the case of ephemeral memoranda could be quickly effaced. Bark and palm leaves were also used for writings of a temporary character, and in some countries in later times both linen and silk have been so employed. The Chinese are credited with the invention of paper anterior to the Christian era, a statement which need not excite surprise when we remember that they anticipated Europe in the invention of printing by nearly a thousand years. We may assume that for many centuries before this the art of writing in China had been brought to some degree of perfection.

Among the Roman antiquities found in Britain, which are now deposited at the British Museum, are many specimens of the stylus in ivory, bronze, &c., and some of these are armed with a sharp projection, with which guiding lines could be ruled across the waxen surface of the tablets. The reed pen was commonly used for writing on papyrus, and the steel pen was foreshadowed by a few specimens in bronze found in Italy, and one in England. This last is among the Romano-British antiquities in the British Museum. It consists of a tubular piece of bronze, about five inches in length, which has at one end a split nib, while the tube is gradually reduced in size towards the other extremity, where it ends in a solid piece, which was probably used for pressing down the wax in order to efface the writing.

In the Mediæval Room at the British Museum may be found many specimens of writing tablets, some dating before the seventh century, of great rarity and therefore great value. Some of these are what is known as "consular diptychs," so-called because these folded tablets were at one time sent as ceremonial presents by the Roman consuls on their appointment to official persons or to friends. Many of these tablets are of ivory and are beautifully carved, and the slabs or plaques are sometimes of such a size that the tusks procurable at the time they were made must have been of unusual dimensions, or the artificers had some means of bending the material, the secret of which is now lost.

Herculaneum Fragments. In 1821 Sir *Humphry Davy* read a paper before the Royal Institution,[1] in which he described a number of experiments that he made with some fragments of papyri which had been found in the ruins of Herculaneum. Of some of these papyri he says: "The black ones, which easily unroll, probably remained in a moist state without any percolation of water; and the dense ones, containing earthy matter, had probably been acted upon by warm water which not only carried into the folds earthy matter suspended in it, but likewise dissolved the starch and gluten used in preparing the papyrus and glue of the ink, and distributed them through the substance of the MSS."

He made further experiments in the Museum at Naples. And of some of the MSS. he says: "These MSS. had been so penetrated by water that there were only a few folds which contained words, and the letters were generally erased, and the charcoal which had composed them was deposited in the folds of the MSS."

He makes some general observations, of which the following is worth noting:

"I looked in vain amongst the MSS. and on the animal (*sic*) charcoal surrounding them for vestiges of letters in oxide of iron: and it would seem from these circumstances, as well as from the omission of any mention of such a substance by *Pliny*, that the Romans, up to this period, never used the *ink of galls and iron* for writing: and it is very probable that the adoption of this ink, and the use of parchment, took place at the same time. For the ink, composed of charcoal and solution of glue, can scarcely be made to adhere to skin; whereas the free acid of the chemical ink partly dissolves the gelatine of the MSS., and the whole substance adheres as a mordant; and in some old parchments the ink of which must have contained much free acid, the letters have, as it were, eaten through the skin, the effect being always most violent on the side of the parchment containing no animal oil."[1]

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[1] *Trans. Roy. Soc.*, 1821, ii. 191.

The disintegration of the papyrus by the action of water, alluded to by Sir *Humphry Davy*,[†] will be readily understood when we remember that this ancient writing material was made of thin strips cut from the reed and cemented together. The strips were laid side by side, and then other strips were laid across them at right angles, the whole being stuck together and placed under pressure so as to form a paper-like sheet. Papyrus was first used as a single sheet, or in lengthy documents as a long roll of different sheets joined together. Later on papyrus leaves were bound together as in a book. At a very early period papyrus was imported into Greece and Italy. It continued to be the chief writing material in Egypt until the tenth century, and was largely used in Europe after vellum had been introduced.

Carbon Inks.—We give illustrations (Figs. 1, 2, and 3) of various writing implements dating back to about 1500 B.C., which are exhibited in the Egyptian department of the British Museum. The titles of these pictures sufficiently explain their nature.

Chinese, or Indian ink, as it is commonly called in this country, was made at a very early period, according to Chinese historians as far back as between B.C. 2697 and 2597, the inventor being one *Tien-Tchen*. Full particulars of the way it is manufactured are given in a subsequent chapter. Its base, like that of early Egyptian and other inks, is carbon.

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[1] *Trans. Roy. Soc.*, 1821, ii. 191.

[†] Several illustrations are attached to Sir H. Davy's paper, mostly showing fragments of papyrus with writing upon them. Fig. 1 shows an ink pot, a reed pen, and a roll of papyrus, and Fig. 2 a box containing roll of papyrus.

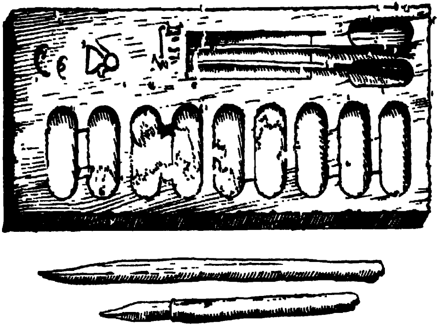

Fig. 1.—Egyptian palette, brushes and pens.

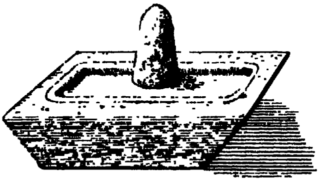

Fig. 2.—Egyptian slab and muller.

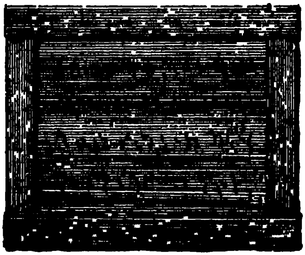

Fig. 3.—Egyptian wax tablet.

Dioscorides,[*] physician to Antony and Cleopatra (B.C. 40–30), in a dissertation on the medicinal use of herbs, gives the proportion of lamp-black and oil to be used in the manufacture of ink (*atramentum*).

Vitruvius,[†] the Roman engineer and architect (B.C. 30 - A.D. 14), describes a method of preparing ink for mural decoration: soot from pitch-pine being collected from the walls of a specially constructed chamber, mixed with gum (*glutinum*), and dried in the sun.

Pliny[‡] (A.D. 23 79) mentions that writing can be readily sponged out, and also speaks of the different varieties of ink in use in his time.[§]

Martial (A.D. 100) sends a sponge with his newly written book of poems, so that the writing could be effaced if the composition did not merit approval.

It is clear from these last two references that an oil-carbon ink cannot be meant, for it would be impossible of removal with water. Either a preparation of lamp-black and gum must be referred to, or possibly an ink made from sepia. *Persius*[¶] (A.D. 34 62) refers to ink becoming too thick and too pale on adding water, and uses the word "sepia." *Cicero*, a century earlier, refers to the use of this natural ink.

Many other natural inks, but of vegetable origin, have been used for writing and marking in various parts of the world. All are fully described later on.

Iron Gall Inks.—The monk *Theophilus*,[**] who wrote an encyclopædia of Christian art in the eleventh century, describes, among other things, a method of preparing writing ink from thorn wood. An aqueous extract of the wood was evaporated to dryness and the powder mixed with green vitriol. This is the earliest reference which we have been able to find to an iron-tannin ink.

A treatise was published in Paris in 1393, under the title of *Menagier de Paris*, in which a method of preparing an iron ink with galls was described.

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[*] Folio edition, 1598, in Greek and Latin.

[†] *De Architectura*, lib. vii. 10.

[‡] *Nat. Hist.* xxvii. § 52.

[§] *Ibid.* xxxv. § 41.

[||] iv. 10.

[¶] *Satires*, iii. 13.

[**] Theophilus, *Diversarum Artium Schedula*, lib. i. chap. xl. p. 48. Hendrie's translation.

Wecker, a doctor of medicine of Basle, in 1612[*] describes the preparation of an indelible ink compounded of lamp-black and linseed oil. He also alludes to coloured inks, and in particular to sympathetic inks.

Peter Canneparius, professor of medicine at Venice, wrote on inks, *De Atramentis*, &c.;[†] and described the composition of various sorts of ink. Black ink is referred to as being made from galls and vitriol, while coloured inks are procured from gums, woods, the juices of plants, &c.

Sir *E. Maunde Thompson* remarks[‡] that ink differs in tint at various periods and in different countries, and that while in early MSS. it is pure black, or slightly brown, in the Middle Ages it varies a good deal according to age and locality. He also tells us that in Italy and Southern Europe the ink of MSS is generally blacker than in the north, and that a Spanish MS. of the fourteenth or fifteenth century may usually be recognised by the peculiar blackness of the ink. The ink of the fifteenth century is often of a faded grey colour.

The Lindisfarne Gospels. The MS. known as *The Lindisfarne Gospels*, or *The Gospels of St. Cuthbert*, or *The Durham Book*, is of great interest, for it is one of the earliest, and certainly one of the most beautiful, MSS. on vellum possessed by the British Museum. Four paintings representing the Evangelists precede the respective Gospels, and three of them are shown in the act of writing. It is noteworthy that the pen, very plainly shown in the figure of St. Mark, is cut like a quill. This MS. is unusually fresh and clean, although according to tradition it was, upon one occasion, lost at sea in a violent storm, and was recovered at low tide by the intervention of St. Cuthbert. The date at which it was written is supposed to be at the close of the seventh century. This valuable MS. is placed in a case next to an MS. of Shakespeare's time; and although one is nearly nine centuries older than the other, the ink of the earlier work is perfectly black and well preserved, while that of the other is very much faded.

With regard to the later MSS. on paper and parchment, and confining our attention to those which are exhibited in the open cases at the British Museum, there is little to complain of in the quality of the ink. The writing is mostly of a rich dark-brown, and we may take it that if an MS. has thus preserved its freshness for three or four centuries the ink may be regarded as permanent enough for all practical purposes. It is interesting to note that in some of these MSS. two different inks have been used on the same page. For instance, we have here the Bible which belonged to Milton, on the first page of which he has entered in his own hand memoranda of the births of himself and members of his family. All the entries are written in a dark ink, with one exception—this is the entry referring to the birth of his daughter Deborah on "the 2nd of May, being Sunday, somewhat before 3 of the clock in the morning, 1652." The ink in this case is very pale, the loss of colour being possibly due to hasty dilution.

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[*] *De Secretis*, lib. xvii. 713.

[†] London edition, 1660.

[‡] *Greek and Latin Palæography.*

Transition from Carbon to Gall Inks. The transition from carbon ink to that made from galls and iron is a very gradual one, and we find many writers deploring the effects of that change. Mr. *Astle*[*] (1803) complains that the modern ink is not comparable with that used by the ancients, and attributes the deterioration to negligence in manufacture. He writes: "Gall-nuts, copperas, and gum make up the composition of our inks, whereas soot or ivory black was the chief ingredient in that of the ancients."

Another paragraph from the same source is worthy of quotation:

"Although paper is now chiefly made from linen rags beaten to a pulp in water, yet it may also be made of nettles, hay, straw, parsnips, turnips, colewort leaves, flax, or of any fibrous vegetable."

This extract, written just a century ago, is interesting in view of the circumstance that linen rags are now only used for the very finest grades of paper. Wood pulp is now largely employed, and there is ground for the fear that in the future it will not be the quality of the ink which will be called into question, so much as the perishing of the material upon which the writing is recorded.

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[*] *Origin of Writing*, 1803, p. 210.

We may also notice here "Some Observations on Ancient Inks,"* which formed the subject of a communication to the Royal Society by Sir *Charles Blagden*. He made experiments on various MSS. on vellum, dated from the ninth to the fifteenth centuries. The ink of some was still quite black, while that of others varied from a deep yellowish brown to a very pale yellow. These were lent him by Mr. *Astle*.

He made several experiments, and convinced himself that the ink used in these MSS. was iron-gall. "No trace of a black pigment of any sort was discovered."

He attributes "the greater durability of the more ancient inks" to the more careful preparation of the parchment or vellum; one writing only resisted all the agents which he employed, and that turned out subsequently to be part of a very ancient printed book.

Perhaps the change of which so many writers complain may be more reasonably ascribed to the want of knowledge with regard to the proper proportions of the ingredients employed in the preparation of ink, which had not yet attained the position of an article of commerce.

Domestic Ink-making.—It is very difficult for us in this twentieth century to realise a time in Britain when the art of writing was a polite accomplishment, only known to a privileged few; when the commercial manufacturer of ink did not, could not exist, for he would have starved through lack of custom. Then it was, that the careful housewife would rank it among her duties to make ink, just as she made cordials, and compounded medicines of marvellous origin for the family use; and we may take it for granted that recipes for the manufacture of writing fluids, sympathetic and otherwise, would be handed down, with other nostrums, as precious heirlooms from generation to generation.

We have evidence of this in an interesting volume which was compiled a few years ago by Mr. *George Weddell* of Newcastle-upon-Tyne.† It is a book of family recipes, which came into his hands by an accident. He has reproduced it in *fac simile*, and it is certainly a most interesting relic of domestic life in the sixteenth and seventeenth centuries. It deals with all kinds of things, good and bad, from recipes for apple pasties to cures for the King's evil. And among the strangely assorted items we find several recipes for making ink. By the kind permission of Mr. *Waddell* we reproduce one of these as a frontispiece: and as few, possibly, of our readers will be able to decipher the strange calligraphy, the gist of a transcription which Mr. *Waddell* has been good enough to supply, is given in chap. iv.

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* *Trans. Roy. Soc.*, 1787, lxxvii. [ii.] 451.

† *Arcana Fairfaxiana Manuscripta*, 1890.

Another recipe in this delightful old volume stands as follows:

"Take a quart of fair spring water, one ounce of copperas, two ounces of gall, and four ounces of gum-arabick mingle them together and let them stand

Here is another method:

"Take four ounces of gum arabick beat small, 2 ounces of gall beat gross. One ounce of copperas and a quart of the comings off strong ale Put all these together and stir them 3 or 4 times a day about 14 dayes then strein it through a cloth.

Then follows this note:

"I made ink by ye above rect. only putting half ye arabick and as good as ever was used.—K. GILES.

One more recipe from the same source is as follows:

"Mr. Mason, Exciseman, his rect. for making ink, which is very good "Take a quart of rain or other soft water and put to it 4 oz. of best blue galls gross by beattin—let it stand warm for 3 days then add 5 oz. of copperas 4 oz. of gum ditto roach (rock) allum let it stand 2 or 3 days longer but shake it up 2 or 3 times a day put a little Brandy into the ink The bottle in it will hinder it from Mouldiness."

There is no date to any of these recipes. Mr. *Waddell*, who has made a study of the different handwritings reproduced in this book, is of opinion that the first of them, our frontispiece, is certainly Elizabethan, and that it was probably written at the end of the sixteenth century by a man past middle age, who learned to write just about the time that Shakespeare was born (1504).

A book on handwriting by *John de Beau Chesne* and *M. John Baildon*, printed at Blackfriars in 1571, entitled

A Booke containing Divers Sortes of Hands, contains "Rules made by E. B. for his children to learne to write bye." They include directions for making ink. These are quaint enough to deserve quotation:

> To make common yncke of Wyne take a quarte,
> Two ounces of gumme, let that be a parte,
> Five ounces of galles, of copres[*] take three,
> Long standing dooth make it better to bee:
> If wyne ye do want, rayne water is best,
> And as much stuffe as above at the least
> If yncke be to thick, put vinegre in,
> For water dooth make the colour more dimme.
> In hast for a shift when ye have a great neede,
> Take woll, or wollen to stand you in steede;
> Which burnt in the fire the powder bette small
> With vinegre or water make yncke with all.
> If yncke ye desire to keep long in store
> Put bay salte therein and it will not hoare.[†]
> If that common yncke be not to your minde
> Some lampblack thereto with gumme water grinde.

In 1609 an iron-gall ink was invented by *Guyot* and sold on the Pont Neuf, Paris, under the title of *encre de la petite vertu*.[‡]

Scientific Experiments.—In the following century, so much more attention appears to have been given to the manufacture of writing ink, that we find a compound known as "the celebrated Dresden ink" being used in Germany. We give further details as to its composition in chap. iv.

William Lewis, M.D.,[§] in 1748, has the credit of being the first to make writing fluids the subject of scientific experiment, and to draw deductions as to the best proportions of the various ingredients required to make a really permanent ink.

Ribaucourt[‖] (1792) carried out experiments on the same lines as Lewis, but arrived at somewhat different conclusions as to the correct proportions of the constituents.

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[*] Copperas, *i.e.*, $FeSO_4$.

[†] A.S. *har*, hoary, gray. Ice. *hárr*. In allusion to the gray colour caused by mould.

[‡] Blondel, *Les Outils de l'Écrivain*, 1890, p. 153.

[§] *Commercium Philosophico-technicum*, London, 1763, p. 377.

[‖] *Ann. Chim.*, 1792, xv. 113.

Unoxidised Gall Inks.—The use of dyestuffs such as logwood or indigo to strengthen the colour of the ink, was practised to a small extent during the eighteenth century; but the inks were still of one type, that is to say, the fluids were more or less oxidised before their application to the paper. In the early part of last century, however, a radical change came about in the method of manufacture, and credit for the innovation is claimed by the well-known firm of *Stephens*. Previously to this, the finished ink was exposed to the action of the atmosphere so as to darken it as much as possible, whereby it was rendered more or less insoluble, and would, therefore, for the most part, remain on the surface of the paper. The new process consisted in keeping the ink from oxidation as far as possible, so that the formation of the insoluble pigment would take place within the fibres of the paper: at the same time indigo was added to give the fluid a "provisional" colour

An unoxidised ink of the same type was patented by *Leonhardi* in Hanover in 1856, a small proportion of madder being incorporated in addition to the indigo. Hence the term *alizarine*, which has been accepted as a descriptive title for this type of ink, although *Leonhardi* subsequently omitted the madder as being superfluous. Attempts to employ the more appropriate term "*isatin*" (indigo) to such inks were unsuccessful, and they are still, on the *lucus a non lucendo* principle, called "alizarine." Other manufacturers have seen the advantages of a non-oxidised ink, and *blue-black* writing fluids are now largely made. In 189[illegible] *Schluttig* and *Neumann* examined eighty-one German inks, and found that all were of the new type—the older kind of ink being obtainable from a few small makers.

Aniline Inks.—The next development in the manufacture of ink is found in the use of aniline dyes, not merely for coloured writing fluids, but also for taking the place of the indigo in the black inks. The first British patent for the employment of these dyes as ink was granted to *Croc*, of Paris, in 1861, and he was followed by several others. Thus, under the name of "Stylographic ink" a solution of nigrosine was introduced in 1867, as being specially suitable, on account of its fluidity, for stylographs and fountain pens.

In 1878, at the Paris Exposition, a medal was given to the makers of an aniline ink which was found capable of great resistance to the action of acids, alkalies, and chlorine.

German Regulations.—In 187[illegible] Professor *Koster*, of Bonn, wrote to the German Chancellor, pointing out the danger of using aniline inks for historical documents on account of their instability; and, as a result of this, Prussia passed a law in the same year enacting that only iron-gall inks should be used officially.

In 1888 rules for testing ink were published, and inks were classified according to the way in which they answered to these regulations. Some of these tests have been severely criticised by *Schluttig* and *Neumann*.

Other Inks—Coloured inks, marking inks, printing inks, and inks for special purposes, need only be alluded to, as they are fully dealt with in subsequent chapters. The interesting question of the detection of forgeries by photographic and other means is also considered at length.

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SECTION I.

WRITING INKS.

CHAPTER I.

CARBON AND CARBONACEOUS INKS.

CONTENTS.—**Sepia**—Source—Manufacture—Chemical composition—Sepiaic acid—British sepia—Examination of commercial sepia—**Indian or Chinese Ink**—Lamp-black—Composition—Manufacture of lamp-black—Old European methods—Manufacture of Indian ink—Qualities of Indian ink—Examination of Indian ink—Practical tests—**Carbon Writing Ink**—Ancient carbon inks—Modern carbonaceous inks.

As was shown in our preliminary historical sketch, inks having carbon or a carbonaceous pigment in a finely divided state for their pigment date back to periods of remote antiquity, though for writing purposes they have to a large extent been superseded, at least in Europe, by inks in which the pigment is more or less in solution.

The inks which may be conveniently considered under this heading comprise (1) Sepia, (2) Indian or Chinese ink, and (3) inks of the type of the ancient writing inks, which contain elementary carbon suspended in a suitable medium.

(1) SEPIA.

Source.—The black or dark brown pigment known as sepia is contained in a secretion formed in a special glandular organ of different species of Cephalopoda, including the common cuttle-fish or squid. The "ink-sac" or "ink-bag," as this glandular organ is popularly called, has strong fibrous walls, and is generally, though not invariably, provided with a separate ejaculatory duct.

Mr. *Martin Duncan*, who has made a study of living members of the Cephalopoda, which he kept in a large tank made for the purpose, stated in a lecture before the London Camera Club, October 15, 1903, that it was not an easy matter to cause a cuttle-fish to exhaust its stock of ink. And the facility with which it would discharge the liquid upon the least provocation was one of the great difficulties with which he had to deal in prosecuting his inquiries; for a whole tank full of water would be clouded

Fig. 4.—Common cuttle-fish (*Sepia officinalis*).

in a few seconds, and work had to be suspended until the vessel had been thoroughly cleaned and refilled. He also stated that an exhausted cuttle had the power of renewing the inky secretion in as short a period as a quarter of an hour.

Fig. 4 represents the common cuttle-fish (*Sepia officinalis*) from which the ink is obtained. By the kindness of the Curator of the Geological Museum, London, we have been able to photograph specimens of fossil Cephalopoda from the Blue Lias in which the ink-bags remain intact. It is a well-known circumstance that this fossil sepia has been more than once ground up with water and found to furnish an excellent ink. This is alluded to in the Bridgewater Treatise by Dean Buckland. In Figs. 4 and 5 the ink sacs are indicated by the white pointers.

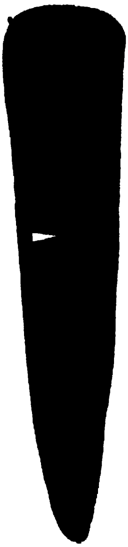

Fig. 5.—Fossil sepia.

Mr. *Henry Lee*, for some time Naturalist to the Brighton Aquarium, writing of this black fluid, says:[*]

"The cuttle (sepia) discharges it on the slightest provocation; and this is sometimes very troublesome and annoying when this species is exhibited in an aquarium. The quantity of water its ink will obscure is really surprising. The fluid is secreted with amazing rapidity, and the black injection frequently occurs several times in succession. I have often seen a cuttle completely spoil in a few seconds all the water in a tank containing a thousand gallons."

The extreme diffusibility of the pigment is also referred to by *Ure*,[†] who states that one part of sepia immediately renders 1000 parts of water opaque. The cuttle-fish is thus provided with a most effective weapon of defence, which enables it to effectually cover its retreat when attacked by its enemies.

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[*] *Aquarium Notes*—The Octopus.

[†] *Dict. of Chem.*—Sepia.

The pigment most highly valued is that obtained from the Mediterranean cuttle-fish, *Sepia officinalis*, and from *S. loligo*, and *S. tunicata*, though it is also prepared from the ink-sacs of other species. The ink-sacs are removed as soon as possible after the capture of the fish, and rapidly dried to prevent putrefaction. It is a common practice for the fishermen on the South Coast of England to remove the ink-bags of the cuttle-fish, whose flesh they use for their bait, and to keep them in a dried condition until they can dispose of them to the manufacturers. A large amount of sepia is also obtained from Ceylon, where the cuttle-fish are collected by natives for a very low daily wage.

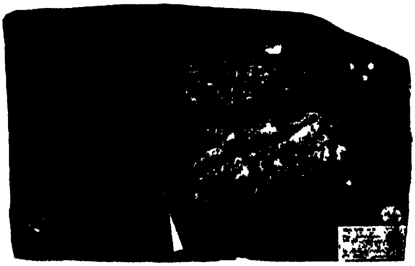

Fig 6.—Fossil sepia.

Manufacture.—There is good reason for believing that ink manufactured from the pigment of the cuttle fish was used as a writing ink by the Romans,* but it is now probably used exclusively in the manufacture of the "sepia" of the artists.

For this purpose the dried ink-sacs are pulverised, and the powder triturated with caustic lye and boiled for thirty minutes. The liquid is then filtered and neutralised with hydrochloric acid, and the precipitated pigment repeatedly washed with water, and dried at a low temperature.

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* Pernies, *loc. cit.*

Modifications of this process are used by different manufacturers, the exact details of which are regarded as trade secrets.

The pigment separated from the other constituents by some such process as described above is ground down to an impalpable powder on a marble slab, usually by manual labour. It is then made up into cakes, or is prepared in a moist condition and put up in pans or tubes, or is incorporated with oil for use as an oil paint.

In purchasing the raw material the manufacturer's chief consideration is to see that the ink-sacs are full, not withered. There does not appear to be much variation in the colouring power of different samples of the crude sepia.

Chemical Composition. — It has frequently been stated,[*] though without justification, that the pigment of the cuttle-fish consists of finely divided carbon associated with proteid substances and calcium phosphate, but it is now known to be a complex organic compound.

Kemp,[†] who examined the liquid from the ink-sac whilst in a fresh state, found that it yielded precipitates with alcohol, mineral acids, tannin, and mercuric chloride. It was very viscous, and possessed a peculiar fishy odour, but little taste. He came to the conclusion that it consisted mainly of albumin, with possibly some gelatin.

Shortly afterwards *Prout*[‡] made a chemical examination of the black residue contained in the dried ink-sac. It was a hard, brittle, brownish-black substance with an iridescent lustre. When powdered, it yielded a violet-black powder without odour, but with a slightly salt taste. Its specific gravity was 1.640. When digested with water for a long time it yielded a brown solution, giving a brown precipitate with lead nitrate. It was found to contain the following constituents: Black pigment (*melanin*), 78 per cent.; calcium carbonate, 10.4 per cent.; sulphates

[*] *E.g.*, in Tomlinson's *Cyclopædia of Useful Arts*, 1854, p. 598.

[†] Nicholson's *Journ. of Nat. Philos.*, 1813, xxxiv. 34.

[‡] *Annals of Philosophy*, 1815, v. 417.

and chlorides of the alkali metals, 2.16 per cent; and mucine, 0.84 per cent.

The melanin was isolated by boiling the black mass with successive portions of water, hydrochloric acid, and dilute ammonium carbonate solution. The residue thus obtained was a black shining powder resembling charcoal in appearance, and emitting a fishy odour when burned. It was insoluble in water, alcohol, or ether, though it remained for a long time in suspension in water. By adding acids or ammonium chloride to the water its separation was accelerated. It was partially soluble in hot potassium hydroxide solution, yielding a brown liquid, from which slight precipitates were obtained with hydrochloric or sulphuric acids, but not with nitric acid. The original pigment was quite insoluble in the two former acids, but dissolved in nitric acid. It was also soluble in ammonium hydroxide, but not in solutions of ammonium carbonate.

A more recent research is that of *Girod*,[*] who made a full analysis of the liquid secreted by the ink-sac of *S. officinalis*. He found it to be odourless, but having a slightly salt taste. When examined under the microscope the liquid was seen to consist of minute corpuscles suspended in a clear serum.

Chemical analysis showed the liquid to consist of 60 per cent. of water; 8.6 per cent. of mineral matter; 30.54 per cent. of insoluble organic matter; and 0.86 per cent. of soluble extractives.

The mineral matter included calcium, magnesium, sodium, potassium, iron, carbonates, sulphates and chlorides, though curiously it was free from phosphates.

The pigmentary substance was obtained in a pure state by digesting the dried residue for four days with alcohol, and then for four days with ether, to remove the extractives. It was then collected on a filter, washed, and digested with glacial acetic acid to eliminate albuminous substances, then with potassium carbonate to remove mucine, and finally with dilute hydrochloric acid (1 : 10) to free it from the mineral salts.

As thus prepared the pigment (after drying at 100 C.) was a black homogeneous substance, leaving no residue of ash on ignition. It was insoluble in water, alcohol, ether, and acids, with the exception of nitric acid. It was bleached by chlorine and by bleaching-powder, and when heated with soda lime evolved ammonia.

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[*] *Comptes Rendus*, 1881, xciii. 96.

Its elementary composition was as follows: Carbon, 53.6; nitrogen, 8.8; hydrogen, 4.04; and oxygen, 33.56 per cent.

Fig. 7.—Dried sepia sacs.

Sepiaic Acid.—In 1888 *Nencki* and *Frau Sieber*[*] obtained an amorphous substance, to which they gave this name, by treating the pigment *melanin* with fifteen times its weight of a 10 per cent. solution of potassium hydroxide. It had the following elementary composition: Carbon, 56.3; hydrogen, 3.6; nitrogen, 12.3; sulphur 0.5; and oxygen, 27.3 per cent. It was found to be soluble in solutions of alkalies, and was precipitated from its solution by copper sulphate and by ammoniacal zinc chloride.

[*] *Chem. Centralbl.*, 1888, xix. 587.

British Sepia.—Through the kindness of Messrs. *Newman* we have been enabled to examine several ink-sacs of cuttle-fish from Southampton, in the dried condition as received by them. The appearance of these is shown in the accompanying figure (Fig. 7). The general physical characteristics were very similar to those recorded by *Prout* (*supra*), but our specimens had the distinct fishy odour observed by *Kemp* in the case of the fresh liquid, and this became very marked on boiling the powdered substance with water.

The powder contained 17.56 per cent. of moisture, and on ignition over a low Argand flame yielded 12.22 per cent. of ash, containing the following constituents: Silica, 0.28; calcium, 1.92; magnesium, 1.75; chlorine (including other halogens), 1.07; sulphuric acid, 1.84; total nitrogen, 8.42 per cent.

When treated with boiling water the powder dissolved to a considerable extent, but repeated and tedious extraction was necessary to remove the whole of the soluble matter. The black residue left on the filter amounted to 71.1 per cent. of the original substance, and contained 7.46 per cent. of nitrogen, calculated on the original powder.

The brown solution when evaporated left a brown resin-like deposit, which on ignition gave 4.55 per cent. of ash, calculated on the original substance.

On treating the insoluble residue with boiling 10 per cent. potassium hydroxide, 19.23 per cent. (calculated on the original substance) remained undissolved.

Examination of commercial Sepia.—Most, if not all, of the English manufacturers prepare sepia exclusively from the cuttle-fish, but there is reason to believe that a large proportion of the so-called "sepia" of foreign origin is sepia in name only.

A chemical means of distinguishing between genuine sepia and preparations consisting of lamp-black or other forms of carbon incorporated with glue consists of treating the powdered sample with boiling water until thoroughly disintegrated, filtering the liquid, and thoroughly washing the residue.

In the case of sepia, this residue will contain a large amount of nitrogen, and on ignition will leave a considerable proportion of ash containing the constituents mentioned in the previous section (p. 22).

Lamp-black preparations, on the other hand, will leave a residue of practically pure carbon, containing only traces of nitrogen, and leaving but little ash on ignition. The whole of the glue, which would cause the finished preparation to show a large proportion of nitrogen, will have been removed by the treatment with hot water and filtration.

The main points to be considered in a manufactured sepia are the colouring power and permanency of the colour.

Sepia was one of the pigments tried in the experiments of Dr. *Russell* and Sir *William Abney* (chap. vi.), and to quote the words of the latter:* "We are apt to look on sepia as one of the most permanent pigments; as a matter of fact it is fugitive, and those who have examined sepia drawings made in the early part of the century will see there has been certainly a distinct fading in those drawings."

2. Indian or Chinese Ink.

The extreme antiquity of the ink manufactured by the Chinese has already been mentioned in the Historical Introduction. According to ancient Chinese documents cited by *Jametel*,† the earliest ink was a kind of vegetable varnish, and it was not till about the third century B.C. that the solid product prepared from lamp black and glue was introduced. The province of Kiang-si enjoyed a monopoly of the manufacture, and the ink attained a high degree of perfection, its quality being maintained by special ink inspectors.

This ink has also been prepared in Japan for many hundred years. The province of Omi produced a fine quality known as *takesu*, but the *taikeibuku* of Yamashiro was considered the best. At the present day the best quality of Japanese ink is said to be manufactured in Nara or Matsuda.

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* *Journ. Soc. Arts*, 1880, xxxvii. 113

† *L'Encre de Chine*, d'après des Documents Chinois, traduits par M. Jametel, Paris, 1882.

Lamp-black: *Composition.*—When carbonaceous products, such as oil, rosin, or tar, are burned with an insufficient supply of air, the oxygen combines with the hydrogen forming water, whilst the carbon is to a large extent deposited in the amorphous form known as lamp-black.

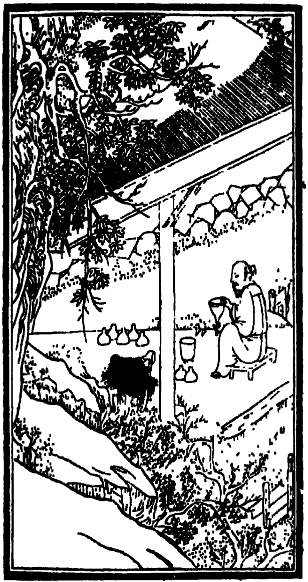

Fig. 8 Chinese manufacture of lamp-black.

The amount of pure carbon in this sort is about 80 per cent., the remainder consisting of oily and resinous substances with inorganic salts, notably ammonium sulphate. For ordinary commercial uses these impurities are not altogether disadvantageous; but if a purer substance is required, the lamp-black is heated to redness in a closed crucible to carbonise the organic substances, and then digested with hydrochloric acid and thoroughly washed with water to remove inorganic salts, the final product being nearly pure carbon. The purest form of lamp-black is obtained by passing a slow current of turpentine vapour through tubes heated to redness, and igniting the deposit in chlorine to remove the last traces of hydrogen.

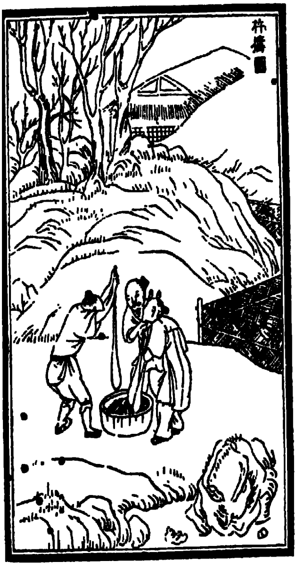

Fig. 9. - Chinese manufacture of ink.

Manufacture of Lamp-black: Chinese Method.—The oldest method of which we have any record is that which has been used by the Chinese for centuries.* Various substances have been used as the original source of their lamp-black, such as rice straw, pine wood, and haricot beans, but these have been for the most part discarded in favour of vegetable oils, and in particular that obtained from the seeds of *Aleurites cordata*, or tung-oil, which yields a brilliant black ink, deepening in tone with age.

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* Jametel, *loc. cit.* p. 11.

The oil is burned in small terra-cotta lamps, which are placed in terra-cotta chambers with a hole to admit air, and having a depression on the top in which water is placed. The smoke is collected in inverted terra-cotta cones with polished interiors, which are fixed above the flame. From time to time the cones are replaced by fresh ones, and the deposited soot removed by means of a feather, care being taken to reject all oily particles.

Figs. 8 and 9 are reproductions of two of the quaint illustrations copied by *Jametel* from ancient Chinese manuscripts.

In some factories the terra-cotta condensing chamber is replaced by a hollow wooden tunnel, having a hole bored in the wall to act as the ventilating shaft. A range of bricks inside supports the cones, of which about twenty are used at a time.

The best season for the manufacture of lamp-black is at the end of autumn or beginning of winter. The terra-cotta condensers are placed in a room carefully protected from draughts, which would interfere with the regular deposition of the soot. The cones are examined hour by hour, since delay in changing them causes the lamp-black to assume a yellow tint.

*Julien** states on the authority of Chinese documents that the finest quality of ink is prepared from the lamp-black obtained from sesamé oil, or from tung oil, whilst the soot of pine wood or deal is used for the commoner kinds.

Strips of pine wood about 18 inches in length are burnt in a bamboo cabin, 100 feet in length, which is covered inside and out with paper, and divided into several compartments by partitions, in each of which is an opening for the passage of the smoke. The deposit in the furthest compartment is the lightest and makes the best ink, whilst that in the first and second compartments is very coarse, and is sold to printers, varnishers, and house painters.

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* *Ann. de Chim.*, 1833, liii. 308.

The quality of the lamp-black has a very great influence upon the character of the ink, and the Imperial ink is prepared from the very lightest and purest that can be obtained.

Old European Method.—Lamp-black is manufactured on a large scale from the resinous impurities obtained as by-products in the manufacture of turpentine, and is also prepared from oil, tar, &c. The initial substance is burned in a furnace with an insufficient supply of air suitably regulated by apertures which can be opened or closed. The dense smoke is conducted through a flue into a cylindrical stone, brick, or cast-iron chamber, the sides of which are covered with sacking or sheep-skin. An iron cone is

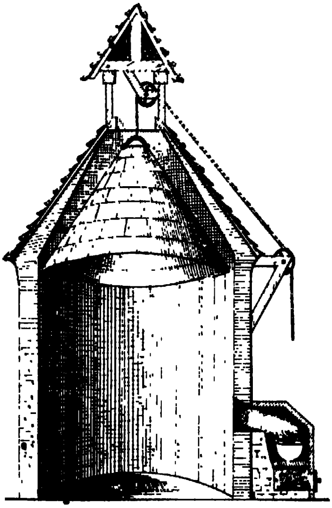

Fig. 10.—European lamp-black chamber.

suspended within the chamber, which it fits so exactly that when lowered its edges scrape the suspended sacking and remove the deposited lamp-black (see Fig. 10).

A small hole in the top of the cone allows the smoke to escape into the chimney of the cylinder, leaving most of its carbon behind. From time to time the suspended sacking is removed, scraped, and replaced.

A more economical method is to conduct the products of combustion first through an iron tube, where oily substances are deposited, and then through a series of iron condensing chambers, where the carbon is deposited, the purest product being obtained from the final condenser. This method of condensing is employed in the manufacture of the finest grades of lamp-black, the source of the smoke being fatty oils burned in lamps.

An impure form of black of bad colour is prepared from certain kinds of coal, and is chiefly used for pitching ships.

Other varieties of black are *Spanish black* from cork; *vine black* from the twigs of the vine; *peach black* from peach kernels; and *German black*, said to be obtained from a mixture of wine-lees, peach kernels, and bone shavings.*

More modern methods of preparing black for printing inks are described in chap. x.

Manufacture of Indian Ink.—The fullest source of information on the Chinese methods of preparing the ink from the lamp-black is still *Chen-ki-Souen's* book as translated into French by *Jametel*. From that we learn that the lamp-black is first sieved into glazed vases, and then dried in paper bags suspended in a dry chamber. The glue is prepared either from fish or from ox-hide, and is used in the proportion of four to five catties† to each pound of lamp-black. If too little glue be used, the ink is blacker, but not so permanent. The solution of the glue is poured through a sieve on to the lamp-black, and the paste thoroughly mixed and heated for fifteen minutes in a tightly closed vessel over boiling water. It is next pounded for four hours in a mortar (see Fig. 9), until the mass becomes thoroughly pliable, after which it is mixed with musk and camphor and beaten into long sticks. These are then moulded into cakes weighing about 14 to 140 grammes, and the cakes dried by desiccation in well-burnt ash from rice straw, which is replaced daily by fresh ash. The desiccation takes from one to three or four days or longer, but if the process be continued too long the ink becomes pale and loses its brilliancy.

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* Lewis, *Philosophico-technicum*, 1763, p. 377.

† A catty = 800 grammes.

The following proportions are given as the best for an ink that will become blacker with age:* Lamp-black from dryandra oil, 10 catties: old ox-hide glue, 1½ catties; old fish glue, ½ catty; extract of sou-mou and another Chinese aromatic plant, 1 catty.

The addition of a small quantity of dried ox-tongue is said to give a violet tint to the ink, whilst finely powdered vegetable matter is added to produce a bluish tint.

The glue must be white and transparent. It was formerly obtained from various substances, such as rhinoceros' and stag's horn, but is now exclusively prepared from ox-hide or from fish. A decoction of the plant *Hibiscus mutabilis* was formerly used, but according to *Jametel* has long been discarded.

At the present day the only essential difference in the ink produced by different Chinese manufacturers is that different proportions and methods of incorporating the chief ingredients are employed.

The methods of preparing Chinese ink, which are given in a history of China published by *du Halde*, a Jesuit missionary,† in 1735, agree in all essential details with the above account. Lamp-black from pine wood or from oil was mixed with glue or with gum tragacanth and aromatic essences, and the paste pounded, and stamped into tablets, which were finally dried for three to ten days in cold ashes.

In Japan the lamp-black is obtained chiefly from sesame oil or from pine wood, and is mixed with ox-hide glue in a copper vessel surrounded by another vessel containing hot water. The plastic mass is beaten in wooden moulds into cakes, which, as in the Chinese method, are dried by contact with absorbent ash.

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* Jametel, *loc. cit.* p. 28.

† *Description de l'Empire de la Chine*. Paris, 1735, ii. p. 245.

Eisler[*] describes a method of preparing Indian ink from animal and vegetable charcoal mixed with milk and thick gum water, and allowed to dry into cakes.

A modern (European) method of preparing Indian ink consists of triturating the lamp-black with a dilute solution of potassium hydroxide, so as to form a cream. This is poured in a thin stream into slightly alkaline water, and the deposit collected, washed with water, dried, and incorporated with a decoction of the seaweed known as Irish moss or carrageen, to which a little musk has been added.

In another process, a solution of gelatin is boiled under pressure for two hours, and then for one hour more. over an open fire until suitably concentrated, and then mixed with lamp-black that has been heated to redness in a closed crucible. The object of heating the gelatin is to convert it into the so-called gelatin-peptone. which does not solidify like ordinary gelatin. Indian ink thus prepared does not gelatinise in cold weather.

Merimée[†] also prepared Indian ink by mixing a strong decoction of galls with a solution of glue, washing the precipitate with water, and dissolving it in a fresh solution of glue, which is then concentrated to the required consistency and mixed with lamp-black. Dextrin is sometimes used in place of gelatin or glue in the manufacture of cheaper qualities.

Lehner[‡] asserts that he has prepared Indian ink of equal quality to the best kinds obtained from China by the following method: Petroleum or turpentine oil is burned in lamps to which the supply of air is limited. The smoke is conducted through a zinc tube, 100 feet in length, the inclination of which is slightly upwards. The soot deposited at the remote end of the tube is in a very fine state of subdivision, and requires but little purification to free it from the tarry matter which, if not removed, would cause the ink to have a brownish tint. For this purpose it is first boiled with nitric acid, then washed with water by decantation, then boiled with strong sodium hydroxide solution, and finally washed and dried.

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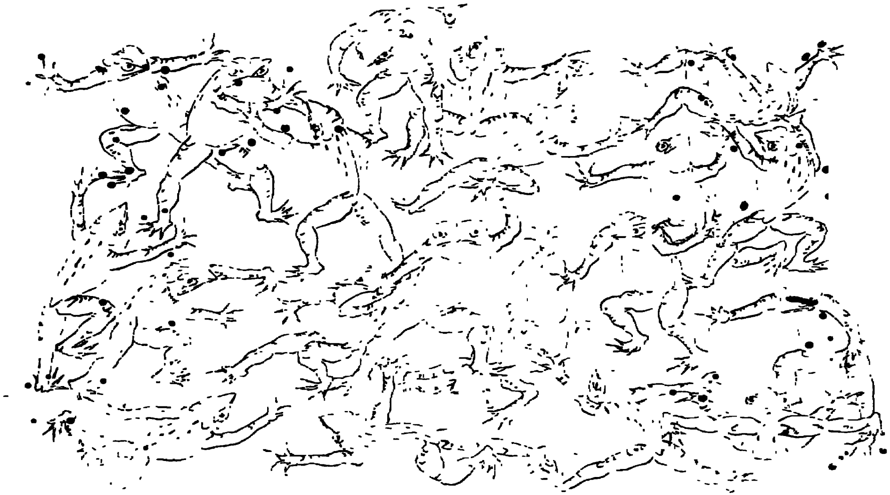
[*] *Dintefass*, 1770, p. 31.
[†] *loc. cit.* p. 197.
[‡] *Die Tinten Fabrikation*, 1880, p. 180.

PLATE I



BRUSH DRAWING IN CHINESE INK BY JAPANESE ARTIST

The purified product, consisting of nearly pure carbon, is mixed into a paste with a clear solution of gum, and heated and stirred until evaporated to the required consistency. It is now allowed to cool gradually, a little tincture of musk being added before it quite sets, and is finally kneaded on a flat plate, and pressed into metal moulds, from which the rods are ejected by tapping.

An inferior kind of ink has been prepared by *Lenher* from ordinary soot purified in a similar manner. This method of preparing ink from purified soot was published long before *Lenher's* book appeared.*

In this country little, if any, Indian ink now appears to be manufactured in the form of cakes. During the war between China and Japan there was a great dearth of the ink, and although some of the largest dealers tried every possible source to obtain a supply, they were unable to do so. From this it would seem that the solid product is now only to be procured from the far East.

This conclusion receives further confirmation from the fact that a large firm dealing in artists' materials now supplies much more of a liquid preparation of lamp-black than of the cakes of Indian ink.

Qualities of Indian Ink.---The ink is imported into England from China in the original boxes, each holding 1 lb. According to the size of the sticks, 8, 20, or 40 may go to the pound, and are spoken of in the trade as "eights," "forties," &c. The sticks are of various forms, some being in squares, some in tablets, and some octagonal. The best qualities of sticks are generally distinguished by being gilt, and are stamped with very fine impressions, such as dragons, lions' heads, &c., which denote different qualities well recognised in the trade. They are obtained from Yutshing and Yenshing.

The octagonal sticks are also of very fine quality. The sticks known as "Mandarin" are of fine quality, and are distingushed from ordinary sticks, which have also a lion on the top, by having a finer impression of the Chinese characters on their sides. The commonest kind are in the form of small sticks with white letters on the side.

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* *Dingler's Polyt. Journ.* 1832, xliv. 237.

Examination of Indian Ink.—Among the Chinese the quality of ink is tested by rubbing the tablet on the palette. If only a faint sound is heard the ink is considered to be of good quality (*Si-mo*), but if a loud noise is produced it is regarded as inferior (*Tsou-mo*).

When rubbed with water, Indian ink should yield a uniform liquid, free from coarse particles or flakes. The best Chinese inks have a brilliant violet shade, whilst inks of the second quality are brilliant black, and inferior inks have a yellow tint. A good ink should not lose its intensity or brilliancy on keeping, and should colour paper a brilliant black. Inferior inks lack either blackness or brilliancy, or both.

A practical test of the quality of an ink made from pine soot was recommended by *Julien*.* This consisted in leaving a fragment in water, and noting the time before it rose to the surface. The better the quality the longer the ink was said to remain submerged.

Practical Tests.—We submitted several of the different grades of Chinese ink to practical tests, first of all reducing each to powder, and immersing 0.1 grm. in 10 c.c. of water. It soon became apparent that the better-class inks were far more readily soluble in cold water than were the cheaper kinds, some of the latter hardly colouring the fluid after some hours' soaking. The various samples were then put in a water-bath and raised to the boiling-point, but the cheaper grades were still more refractory than the others, and required to be rubbed down in a mortar before the particles of carbon were diffused in the liquid. After allowing the containing bottles to rest for an hour, it was found that the sediment of the best samples of ink was of a much finer character than that of the others.

Our next experiment was to test the tinctorial value of the different samples by applying the solutions to Whatman paper, first of all with a full brush covering a long strip of paper while it was pinned on a sloping drawing-board. Each strip of paper was treated with a different sample of ink, and when the first coat was dry, a second was applied, not covering the whole of the strip, but leaving a small portion at the end with the first coating untouched. A third, fourth, and fifth coat followed, each falling short of the preceding one, until at the end of the strip a strong black represented the sum of all. A glance at the results at once showed the advantage of employing the better class of ink, for the cheaper kinds were by comparison lacking in covering power, and there were present particles of carbon which gave rise to streaks under the brush. The best inks worked far more smoothly than the inferior kinds, and opacity was reached with fewer washes. And from what has been already stated it will be evident that in the better class of material the labour of rubbing down the pigment from the solid stick is reduced to a minimum. From our examination of the sediment formed in the inks under examination, it would seem that in the better grades lamp-black of much finer quality is employed than is used in the manufacture of the cheaper kinds.

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* *Ann. de Chim.*, 1833, liii. 314.

These sticks of Chinese ink are exceedingly brittle, and those rendered unsaleable by breakage are commonly ground up in water to form the liquid ink so much employed by draughtsmen and artists in "black and white."

Chemical Composition of Commercial Indian Inks. –The specimens of the four grades of ink submitted to the practical tests described above gave the following results on analysis:

Indian Ink.	Water Per cent.	Carbon residue. Per cent.	Nitrogen in residue. Per cent.	Nitrogen in Original Ink. Per cent.	Ash. Per cent
I. Octagonal stick . .	8.16	53.9	0.0	7.74	4.08
II. Lion stick, fine letters . .	7.20	52.53	--	4.87	3.60
III. Lion stick, coarse letters . .	9.93	49.64	—	7.26	4.96
IV. Small stick, coarse letters . .	9.40	57.04	-	6.84	4.01

The fact that the residue left, on extracting the soluble substances with hot water, is free from nitrogen, affords simple means of distinguishing between Indian ink and pure sepia (see p. 22).

3. Carbon Writing Inks.

Ancient Carbon Inks.—The characters on Egyptian papyri and in Latin and Greek MSS. are frequently much darker and more distinct than those written centuries after with modern iron-gall ink. The latter can be readily destroyed by various chemical agents, such as acids and bleaching agents, and their permanency is also largely dependent on the relative proportion of iron and tannin in the ink, and on the manner in which they have been kept.

Astle, who was Keeper of Records in the Tower of London, and thus had exceptional opportunities of studying MSS. of all ages, found that the black ink used by the Anglo-Saxons in documents of the seventh, eighth, ninth, and tenth centuries had preserved its original intensity much better than that used at later periods, especially in the sixteenth and seventeenth centuries, which was frequently very faint. It was rare to find faded writing in documents before the tenth century. *Astle* * came to the conclusion that this was due to the earlier inks containing carbon; but *Blagden*, on testing the writing with potassium ferrocyanide, found that iron was present in every instance.†

It is impossible to determine the exact period when carbon inks were replaced by iron-gall inks, though it was probably early in the present era (*cf. Historical Introduction*).

The ink of the Greeks and Latins, like the modern Oriental inks, was a mixture of finely divided carbon with a solution of gum or glue, sufficiently dilute to flow from a reed. In reality they were only modifications of the Chinese inks described above, and in some cases were even dried before use. Thus *Vitruvius*‡ states that *atramen-*

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* *Origin of Writing*, 1803, p. 209.

† *Trans. Roy. Soc.*, 1787, lxxvii. [ii.] 451.

‡ Lib. vii. § 10.

tum was prepared from the soot of pitch pine collected on the walls of a marble chamber, mixed with gum (*glutinum*) and dried; and Dioscorides * gives the proportions of soot to gum as three to one.

Evidently the brilliancy of the black deposit and the more fluid character of iron-gall inks led to their gradually superseding carbon inks for writing purposes, of which no mention is made in mediaeval literature.

It is true that *Werker* in 1582 gave a formula for an *atramentum perpetuum*, but this was really a printing ink consisting of linseed oil and lamp-black, and there is no reference to an aqueous carbonaceous ink in his book or in that of *Canneparius* (1660).

Modern Carbonaceous Inks.—*Lewis* † in 1764 made various suggestions for rendering ink more permanent, some of which are described more fully in chap. xiv. His principal plan was to add finely divided lamp-black or ivory black to a good iron-gall ink, but such ink could be bleached by chemical means to destroy the gall ink and then washed with water to remove the carbon.

Other chemists have made use of an essential oil, or of a varnish or saponified resinous substance, or a solution of gluten, to retain the carbon in suspension. Of various old formulae on these lines mention may be made of the following:—

Westrumb's Ink.‡—Galls, 3 parts; Brazil wood, 1 part; water, 46 parts. Boil until reduced to 32 parts. Strain and add ferrous sulphate, 1½ part; gum arabic, 1¼ part; indigo, 1¼ part; and lamp-black, ¾ part.

Close's Ink.§—Powdered copal (25 parts), in lavender oil (200 parts), mixed with lamp-black (2½ parts), and indigo (½ part). If too thick the ink was thinned with turpentine.

Sheldrake's Ink.‖—A mixture of asphalt dissolved in turpentine with amber varnish and lamp-black. The whole question of the best means of rendering writing safe from attempts to remove it is discussed in chap. xiv.

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* *Opera*, lib. v. cap. 183.

† *loc. cit.*

‡ Nicholson's *Journ. of Nat. Philosoph.*, 1802. iv. 479.

§ Nicholson's *Dict. of Chem.*, 1820

‖ *Ibid.*

CHAPTER II.

TANNIN MATERIALS FOR INKS.

CONTENTS.—**Galls**—Origin—Aleppo galls—Chemical composition—Chinese galls—Chemical composition—Japanese galls—Acorn galls—Oak-apple gall—Other galls. **Tannins**—Classification of tannins—Suitability of tannins for ink-making—**Chestnut bark and wood**—Chestnut extract—Chestnut tannin—Ink from chestnut wood—**Sumach**—Sumach tannin—Ink from sumach—**Divi-divi**—Divi-divi tannin—Ink from divi-divi. **Myrobalans** — The tannin of myrobalans—**Valonia**—The tannin of valonia—Ink from valonia. **Oak-bark tannins**—Reactions of oak tannins—Amount of tannins in oak bark—Ink from oak bark. **Gallotannic acid**—Fermentation of gallotannic acid—Properties—**Gallic acid**—Properties—Reactions distinguishing between gallotannic and gallic acids.

GALLS.

Origin.—Curious vegetable excrescences, known as galls, are frequently formed upon the branches, shoots, and leaves of trees, and especially upon the oak. They are produced by the female of certain species of insects, of which the best known are the hymenopterous gall-wasps (*Cynipidæ*), which puncture the young tissues and deposit their eggs. Under this stimulus the plant juices accumulate at the point of puncture, and a gall is gradually formed, which serves as the home of the larva. It is possible that some virus injected simultaneously with the egg plays a part in the development of the gall, but the main essential appears to be the presence of the living larva. Should the egg of the insect perish from any cause no gall is formed, or if the larva dies the gall ceases to grow.

Galls vary greatly both in size and shape, some, *e.g.*, the Californian "flea seed," being very minute, whilst others, like the large galls on the roots of certain oaks, are several inches in diameter. Some galls are round and smooth like the English oak-apples; others, like the Aleppo galls, are crowned with protuberances; whilst others again assume fantastic forms, as in the case of the "artichoke gall" found on certain French oaks, the curious English galls shown in Figs. 11, 12, and 13, and the Chinese and Japanese galls (Figs. 17 and 18). The forms and colours of the different kinds of galls are remarkably constant, and afford a means of distinguishing between the insects, often of very similar appearance, that produce them.

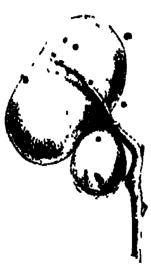

Fig. 11.—English double oak-apple gall.

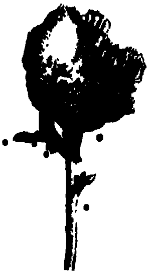

Fig. 12.—English oak gall.

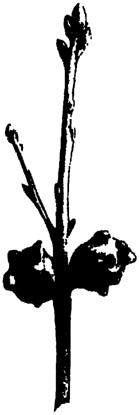

Fig. 13.—English gall.

In the majority of cases galls contain only one larva, and are described as "monothalamous," whilst others afford shelter and food to a colony of larvæ, and the term "polythalamous" is applied to them.

Aleppo Galls.—The ordinary *nutgalls* of commerce are commonly known as *Aleppo*, *Turkey*, or *Levant galls*. They are produced by the female of a gall wasp, (*Cynips gallæ tinctoriæ*, upon the branches of a small oak, *Quercus infectoria*, which is abundant on the Syrian coast, and on the east of the River Jordan. The insect pierces its way out of the gall after five to six months, and the uninhabited galls are then known as *white galls*, from their pale colour. These contain considerably less tannin than galls which still enclose the larva, and have therefore a smaller commercial value. The best galls are selected ahead and harvested before the insect escapes, and from their colour are known as *blue* or *green* galls.

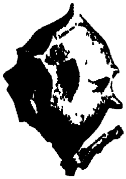

Fig. 14.—Green Aleppo gall.

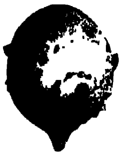

Fig. 15.—White Aleppo gall.

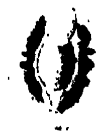

Fig. 16.—Section of white gall.

The value of a given sample of galls depends to a large extent upon the proportion of white galls it contains. Hence, fraudulent attempts are sometimes made to artificially close the holes left by the insect, and so make the galls to appear to still contain the larva.* A section of the nut would readily detect this fraud (see Fig. 16). Aleppo galls vary somewhat in size, but usually average from 8 to 1·5 mm. in diameter. They are globular or pear-shaped, and are crowned with numerous tubercles (Fig. 13). The colour ranges from greenish black to pale

Allen, *Commercial Organ. Anal.*

yellowish green, whilst the interior is pale brown or yellowish green.

The appearance of *white* galls is shown in Fig. 15, and in section in Fig. 16, the latter showing the small canal through which the insect made its way to the surface.

When a thin section of an inhabited gall is examined under the microscope it is seen to consist of an external layer of small cells, forming a sort of bark: beneath these are cellular layers of parenchyma, some of the cells containing tannin and chlorophyll; then come radial cells surrounding the central cavity, in which lies the larva in the midst of an alimentary mass.

Smyrna galls appear to be a commercial variety of Aleppo galls, being somewhat larger and darker in colour, and often containing a larger proportion of white galls.

Chemical Composition.—By treating 500 grains of the best Aleppo galls with distilled water, *Davy*[*] obtained an infusion of specific gravity 1.068, containing 185 grains of solid matter, consisting of 70.27 per cent. of tannin; 16.75 per cent. of impure gallic acid; 6.48 per cent. of gum and other extractives; and 6.50 per cent. of salts of calcium and other metals. From the results of tannin determinations made by later chemists there appears to be little doubt that Davy had not extracted the whole of the soluble constituents of the galls, for on this basis the insoluble woody fibre amounts to 63 per cent. of the total substance.

In 1845 *Guibourt*[†] made a very exhaustive examination of Aleppo galls; and his results, still quoted as final in text-books, are as follows: Tannin, 65.00; gallic acid, 2.00; ellagic and luteogallic acids, 2.00; chlorophyll, 0.70; brown alcoholic extract, 2.50; gum, 2.50; starch, 2.00; woody fibre, 10.50; sugar, proteid, potassium and calcium salts, 1.30; and water, 11.50 per cent.

A later, though less complete, analysis is that of *Watson Smith*, who found Aleppo galls to have the following composition: Tannin, 61.65; gallic acid, 1.60; woody fibre, 15.68; water, 12.32; and colouring matter and loss, 8.75 per cent.

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[*] *Trans. Roy. Soc.* 1803, xciii. 233.

[†] *Archiv. der Pharm.*, 1846, li. 190; *Hist. Nat. des Drogues*, 1849, ii. p. 286.

Buchner[*] obtained the following amounts of extractive matter by treating the powdered galls with different solvents:

		Per cent
Substances extracted	by ether	77.00
" "	by ether and alcohol .	80.40
" "	by cold water . .	86.50

A specimen of commercial nut-galls examined by us contained 44 per cent. of tannin, determined as gallotannic acid by the method described in chap. iii.

Chinese Galls.—The curious variety of galls exported from China are not formed by a gall-wasp like most of the commercial galls, but are produced by a small aphis (*Aphis Chinensis*) upon the leaf, stalks, and shoots of *Rhus semialata*, a tree growing abundantly in sandy places in Northern India, China, and Japan.

The aphis is about $\frac{1}{20}$ of an inch in length by about $\frac{1}{10}$ in breadth at the base of the abdomen, which gradually widens out from the thorax (see Fig. 19, p. 45).

The gall is at first dark green, and gradually changes to yellow before the larva escapes through the walls bursting open, the Chinese peasants collecting them shortly before the change takes place. The aphides are killed by exposing the galls in osier baskets to the action of steam.

The gall is naturally covered with a light powder termed "salt powder" by the Chinese, and used by them for flavouring soup and as a medicine.[†] As imported into Europe the galls are pale grey in colour, and have a hornlike appearance, and a curious odour resembling that of freshly tanned leather (*Hepworth* and *Mitchell*). They vary greatly both in size and in form, but a characteristic shape is shown in Fig. 17. They have a horn-like texture, and when broken open present a hollow interior containing a little chalk-like dust with darker particles, which when examined under the microscope are seen to be dried aphides.

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[*] *Rep. f. Pharm.*, 1851 [3], vii. 373.

[†] Pereira, *Pharm. Journ.*, 1844, iii. 384.

According to *von Rehling*[*] an average-sized gall contains more than 3000 aphides, and by treating the débris with warm water these swell up to about $\frac{1}{25}$ of an inch in size.

Du Halde[†] gives a description of these galls, which, he states, are termed *ou-pey-tse* by the Chinese and are used by them in the preparation of various medicinal compounds. He also states that their formation is due to a small insect.

Chinese galls were first imported into Europe in the eighteenth century under the name of "Oreilles des Indes," but they did not become a regular article of commerce until about 1850. They are now largely used in Germany and America as the raw material for the manufacture of tannic acid, and they form one of the principal and cheapest tannin materials for the manufacture of ink. In fact, according to *Dieterich*,[‡] gall inks are now prepared from them almost exclusively in Germany.

Buchner[§] compared their commercial value with that of ordinary gall-nuts. In 1851 good average blue Aleppo galls cost 100*s.* to 105*s.* per cwt., whilst Chinese galls fetched 65*s.* to 68*s.* per cwt. Thus, taking into account the amount of readily soluble tannin in the latter, they were 1⅓ to 1½ times cheaper than Aleppo galls.

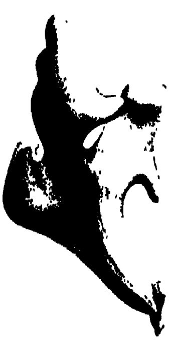

Fig. 17. Chinese gall.

Chemical Composition.—Specimens of Chinese galls were examined in 1817 by *Brande*,[‖] who found them to yield 75 per cent. of soluble matter to cold water, the residue consisting of woody fibre with 4 per cent. of resinous matter soluble in alcohol. The residue from the aqueous extract was found to consist mainly of tannic acid with a little gallic acid.

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[*] *Archiv. f. Chem.*, 1855, cxxxi. 280.

[†] *Description de l'Empire de la Chine*, 1735, p. 496.

[‡] *Pharm. Manual*, 1897, p. 680.

[§] *Rep. f. Pharm.*, 1851 [3], vii. 329.

[‖] *Trans. Roy. Soc.*, 1817, cvii. 39.

From the absence of extractives (gums, &c.), *Brande* concluded that these galls would not be suitable for tanning purposes, and, in fact, he found that leather prepared with them was very brittle when dried. On the other hand, he found this property rendered them particularly suitable for the manufacture of ink, and the ink prepared from them proved to be less liable to become mouldy than that from ordinary galls.

In 1849, *Stein** described a variety of Chinese galls as possessing an odour of tobacco, and containing the following constituents: Ash, 2.00; tannic acid, 69.14; other tannins, 4.0; green saponifiable fat, 0.97; starch, 8.20; woody fibre, 4.9; and "inert" matter, 12.96 per cent.

The tannin was completely extracted by boiling the powdered galls three times with eight times their weight of water. It was regarded by *Stein* as identical with the tannin of ordinary galls.

The ash contained potassium, calcium, magnesium, iron, chlorine, and phosphoric acid.

Bley's† results are similar to those of *Stein*, viz., gallotannic acid, 69.0; resin and fat, 3.0; gallic acid, extractives and proteids, 4.0; starch, 7.35; woody fibre, 8.65; and water, 8.0 per cent.

Buchner's‡ analysis in 1851 gave the following results: Tannic acid, 76.97; fat and resin, 2.38; extractives soluble in water and some salts, 0.89; gums and salts, 5.94; and starch, woody fibre and mineral matter, 13.82 per cent., calculated upon the substance dried at 100 C.

When extracted with ether these galls yielded 79.35 per cent. of soluble matter, of which 76.97 per cent. (on the original substance) dissolved in water. *Buchner* was unable to confirm *Stein's* conclusion as to the presence of other tannins in addition to gallotannic acid. He also came to the conclusion that the tannic acid was identical with that of oak-bark, and that gallic acid was only present in the galls in very small proportion. The mineral matter was found to consist principally of magnesium phosphate.

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* *Dingler's polyt. Journ.*, 1849, cxiv. 433.

† *Archiv. d. Pharm.*, 1850, cxi. 297.

‡ *loc. cit.* p. 323.

Tannic Acid.—The proportion of tannic acid found by *Stein*, *Bley*, and *Buchner* is substantially the same when calculated upon the dried substance, viz., *Stein*, 79.43 per cent.; *Bley*, 75 per cent.; and *Buchner*, 76.97.

Viedt * gives the proportion of tannic acid in Chinese galls as about 72 per cent., whilst *Ishikawa* † found 77.4 per cent.

Samples recently analysed by the authors ‡ have given the following results: Moisture, 10.70; ash, 1.43; and substances soluble in water, 78 per cent. The tannin determined by *Procter's* method was 68 per cent.

Viedt (*loc. cit.*) asserts that Chinese galls do not contain the necessary ferment for the conversion of the gallotannic acid into gallic acid, and that therefore they cannot be used for the manufacture of ink unless a small proportion of Aleppo galls or of yeast be added to the infusion.

We are unable to confirm *Viedt's* statement, which is also altogether at variance with the results obtained by *van Tieghem*,§ who has clearly demonstrated that the conversion of tannic acid into gallic acid is brought about not by a pre-existing ferment, but by the action of certain mould fungi.

We have prepared ink by adding ferrous sulphate to a decoction of Chinese galls without any addition of either yeast or other galls, and found that it behaved just like ordinary gall-ink, giving a writing which rapidly became black on exposure to the air.

Moreover, insoluble deposits formed on exposing the ink to the air, and these deposits contained 6.86 to 7.56 per cent. of iron, results very near to those obtained with ink from gallotannic acid or ordinary Aleppo galls.

Japanese Galls.—These galls are closely allied to the Chinese galls, and are frequently stated to be identical with them. They are produced by *Aphis Chinensis*, or an allied aphis upon the shoots of *Rhus japonica* (Siebold) or *Rhus javanica* (Murray). (See Fig. 20, p. 45.) They must, however, be regarded as at least a distinct variety, and in fact they are so recognised in commerce, though for ink manufacture the two varieties are used indiscriminately. According to *Procter** the Japanese galls are smaller and paler, and are usually more esteemed.

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* *Dingler's polyt. Journ.*, 1875, ccxvi. 453.

† *Chem. News*, 1880, xlii. 274.

‡ Unpublished.

§ *Comptes Rendus*, 1867, lxv. 1091.

Ishikawa † states that considerable quantities of Chinese galls were formerly imported into Japan, but that in 1880 only the native product was used. The Japanese galls (*Kibushi*) are plucked from the trees between July and September, and are placed in boiling water in wooden tubs for thirty minutes, and then dried in the sun for three to four days. They are stored in warehouses in Kiyoto, often for several years, before being used. The reactions given by the tannin they contain are identical with those of ordinary gall-nut tannic acid.

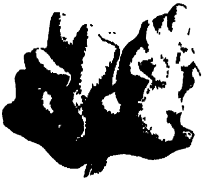

Fig. 18.—Japanese gall.

The amount of tannin determined by the permanganate process in seven samples of different ages up to eight years ranged from 58.82 to 67.7 per cent. The old galls were very brittle, and gave much darker decoctions than the fresh galls, but did not contain less tannin.

The commercial Japanese galls that we have had the opportunity of examining ‡ undoubtedly differed both in size and shape from the Chinese product, were also softer, and had very much thinner walls. A typical Japanese gall is shown in Fig. 18. These galls contained 10.46 per cent. of moisture, 1.96 per cent. of mineral matter, and yielded 50 per cent. of tannin when boiled for three hours with successive portions of water.

Mr. *R. M. Prideaux*, who has kindly made a microscopical examination of the débris in some of these Chinese and Japanese galls, informs us that the two aphides are not demonstrably of different species. Those from the Chinese galls were uniformly smaller than those from the Japanese galls, and lacked the rudimentary wings of the latter; but it would be necessary to follow out the entire life history of both in the growing galls before being able to determine with any certainty the *specific* value of the differences observed in the dead débris. (See Figs. 19 and 20.)

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* *Text-book of Tanning*, p. 28.
† *Chem. News*, 1880, xlii. 275.
‡ Unpublished results.

Acorn Galls (*Knoppern*).—These galls, also known as *Piedmontese galls*, are produced by the female of *Cynips quercus-calicis* on different oaks (*Q. pedunculata*, *Q. sessiflora*, &c.), in the forests of Austria and Hungary, especially in Dalmatia, Slavonia, and Croatia. It is a large gall, 35 to 50 mm. in length, by 35 to 40 mm. in breadth, resembling Aleppo galls in having a crown of five or six points at the top. The interior is spongy, and has a spheroidal chamber containing the larva in the centre. This gall is the same as the *pomme de Chêne* of *Réaumur*.*

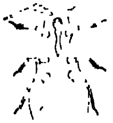

Fig. 19 Aphis from Chinese gall. × 18

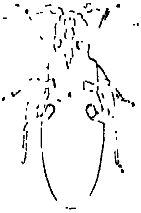

Fig. 20 —Aphis from Japanese gall. × 18

The galls are collected from August to October, after they have fallen from the trees, and are sold either whole or in the form of powder, or as an extract. They contain less than 45 per cent. of tannin, which, according to *Löwe*,† is the same as that of other galls, giving analytical results corresponding with the formula, $C_{14}H_{10}O_9$.

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* *Dict. des Sciences Medicales*, art "Galles.

† *Zeit. anal. Chem.*, 1875, xiv. 46.

Eitner[*] made an examination of the Knoppern collected in 1884 in different districts of Austria, and found them to contain about 12 per cent. of moisture, whilst the proportion of tannin ranged from 23.94 to 35.02 per cent.

Knoppern galls are sometimes used in the manufacture of ink, though according to *Viedt*[†] their use is not common, probably owing to their comparatively low proportion of tannin.

A similar gall is also produced on the *Quercus infectoria* of Asia Minor, but is spherical, and has the tubercles round the centre instead of at the top.

Oak-Apple Galls.—The common galls known in England as *oak apples* are produced by a species of *Cynips* on the branches of the oak, *Quercus robur*, and appear to be closely allied to, if not identical with, the galls formed on that oak throughout Central Europe.

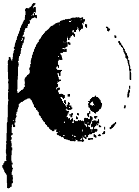

Fig. 21.—Oak-apple gall.

They are perfectly spherical (see Fig. 21), and of a light greyish-green or reddish colour.

British galls contain very much less tannin than Aleppo galls, and generally less than Knoppern. *Braithwaite*[‡] obtained only an insignificant amount from Devonshire galls, but did not state what method of determination he employed.

In 1856 *Vinen*[§] made an examination of the galls produced by *Cynips quercus petioli*, after the escape of the insect. 100 parts of the galls digested with ether and water gave 26.74 parts of extract, containing 17 parts of tannic and gallic acids. According to *Vinen* these galls were at that time used in Devonshire for the manufacture of ink.

In 1847-48 the oaks in East Devonshire became infected with *Cynips Kollari* (Fig. 23), and the galls also appeared suddenly in 1860 in great quantities in the woods to the North of London. According to *D'Urban*[*] these galls contained a considerable amount of tannin and made excellent ink.

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[*] *Dingler's polyt. Journ.*, 1885, cclv. 485.
[†] *Ibid.* 1875, ccxvi. 453.
[‡] *Pharm. Journ. Trans.*, 1855, xv. 544.
[§] *Ibid.* 1856, xvi. 137.

As there was considerable doubt as to the commercial value of British galls, and conflicting statements had been published as to the amount of tannin contained, *Judd* made a series of experiments on galls at different seasons, the tannin being precipitated in each case by means of alum and gelatin.[†] He found that old galls hanging on the trees in December contained on the average 15.97 per cent. of tannin, whilst mature imperforated galls gathered in August contained on the average 17.65 per cent., and half-developed and shrivelled galls 13.44 per cent.

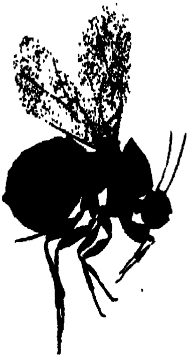

Fig 22.—Gall wasp (*Cynips Kollari*). × 5½.

An ink of average quality was prepared from the old perforated galls.

An analysis of a specimen of Cheshire galls made by *Watson Smith* in 1869 gave the following results: Tannin,

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[*†] *Pharm. Journ. Trans.*, 1863, xxii. 520.

26.71; gallic acid, trace; woody fibre, 47.88; moisture, 20.61; and colouring matter and loss, 4.80 per cent."

"Specimens of old oak-apple galls collected by us during the winter in Surrey contained only 12 per cent. of tannin as determined by *Procter's* hide-powder method, but when examined by a colorimetric method the amount of gallic and tannic acids in terms of gallotannic acid was 30.7 per cent.

These galls yielded a good ink, and there seems to be no reason why English galls should not be used in admixture with the richer foreign varieties by ink manufacturers.

The *French galls* sometimes met with in commerce are slightly larger than ordinary oak-apples, which they closely resemble in general appearance. They are formed upon the shoots of *Quercus ilex* in Mediterranean districts. Probably some of the varieties of Punjâb galls are obtained from this species of oak.

Other Varieties of Galls.—There are numerous other kinds of galls, some of which are of considerable importance as tanning materials, but they do not appear to have been used in the manufacture of ink, though probably some of them would be suitable for the purpose.

The *small-crowned Aleppo galls*, which are occasionally found mixed with ordinary Aleppo galls, are also produced upon *Quercus infectoria*, but by a different insect (*C. polycera*). They are about the size of a pea, and have a circlet of small projections at the top.

Pistachio galls are produced by *Anopleura lentisci* on plants of the *pistacia* order, and are exported from Bokhara together with pistachios. They are red galls, about the size of a cherry, and have a characteristic taste.

Mecca or *Bassorah galls* are produced upon an oak by *Cynips insana*. According to an analysis by *Bley*,* they have the following composition: Tannic acid, 26.00; gallic, 1.60; fatty oil, 0.60; resin, 3.40; extractives and salts, 2.00; starch, 8.40; woody fibre, 46.00; and moisture, 12 per cent.

Tamarix galls, also known as *red galls*, are formed on *Tamarix orientalis* and other plants of the same order.

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* *Archiv. der Pharm.*, 1853, lxxv. [2], 138.

They are of a bright red colour, and are about 1 cm. long by 0.5 cm. broad. They are extensively employed in dyeing and tanning, and in India they are used medicinally by the natives. Similar galls are produced on *T. articulata* in Morocco.

The galls formed on the American "live oak," *Q. virens*, contain 40 per cent. of tannic acid, and are very similar to Aleppo galls. A soft, spongy, and very astringent gall is formed on the Californian oak, *Q. lobata.**

Terebinth galls are due to the action of aphides on certain species of *Terebinthaceæ* growing in the countries bordering on the Mediterranean. They are red in colour, long and flat, and have horn-shaped projections. Within them is a large cavity in which fragments of the aphides can usually be discerned. They contain a considerable amount of tannin and a resinous juice that readily exudes. These galls are sometimes termed *apples* or *galls of Sodom*.

Watt† states that the galls produced upon *Pistacia terebinthus* in India are regarded by the natives as valueless, though the leaves are used for dyeing and tanning. They are sold in Bombay as pistachio galls.

TANNINS.

The substances to which the general name "tannin" has been applied are compounds possessing certain common chemical and physical characteristics. They are widely distributed throughout the vegetable kingdom, and it is not improbable that many of them are individual substances, just as are the different fatty acids that occur in vegetable oils.

When separated in a state of purity or approximate purity, tannins are odourless white or brown substances, with a very astringent taste. They are insoluble in chloroform and carbon bisulphide, but dissolve in water, alcohol, and ether. They yield blue or green insoluble compounds with iron salts, and most of them are precipitated by potassium chromate. They also usually combine with antimony, with lead, and many other metals to form insoluble salts. With lime water they yield precipitates of varying colour, and with gelatin they form an insoluble compound (leather).

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* Trimble. *The Tannins*, vol. i p. 63.

† *Dict. of Economic Products*.

Tannins are soluble in concentrated sulphuric acid, the solution on heating becoming first red (rufigallic acid) and then black (metagallic acid). They are oxidised by nitric acid and by potassium permanganate, the latter reaction forming the basis of a quantitative method of determination.

Classification of Tannins.—Tannins are frequently described as "iron-blueing" or "iron-greening," according to the colour of the precipitate they form with iron salts. This difference is evidently one of constitution, for, as *Stenhouse** first showed, one group of tannins can be converted into gallic acid and yield pyrogallol, whilst the other group does not give these reactions.

Thus, when heated to 160° C., different products of decomposition are formed, the "iron-blueing" tannins, of which gallotannic acid may be taken as the type, yielding metagallic acid and pyrogallol, whilst the "iron-greening" tannins produce metagallic acid and catechol.

Thorpe's method of preparing pyrogallol by heating gallotannic acid in glycerin has been used as a qualitative test of the nature of the tannin: 1 grm. of the tannin is slowly heated to 160° C. in 5 c.c. of glycerin, and the temperature then raised to 200–210° C. for 20 minutes. The liquid is then diluted with 10 c.c. of water and extracted with an equal volume of ether (or extracted with ether without previous dilution, *Trimble*), and the residue from the ethereal extract dissolved in water and tested for pyrogallol or catechol by the following tests:†

Reagent.	Pyrogallol. 1 per cent. solution.	Catechol 1 per cent. solution.
Ferric chloride	Red, turning brown.	Green colour.
Ferric acetate . .	Dark purple	" "
Lime water . .	Purple, then brown.	Clear red
Pinewood moistened with hydrochloric acid . . .	No change	Violet colour.
Melting-point .	131° C.	111° C.

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* *Mem. Chem. Soc.*, 1842, i. 133.

† Trimble, *The Tannins*, i. p. 26.

When a tannin is heated with dilute hydrochloric acid (2 per cent.) in a sealed tube at 100 C. an insoluble precipitate of ellagic acid (crimson colour with nitric acid) may be formed.

When boiled with alkalies the "iron-greening" tannins yield protocatechuic acid and phloroglucinol, or acetic acid, whilst the "iron-blueing" tannins are converted into gallic and ellagic acids.

The elementary composition of the different tannins has been suggested by *Trimble** as a possible means of classification. Thus, the gall tannins, or "iron-blueing" group, contain about 52 per cent. of carbon and about 3·5 per cent. of hydrogen, whilst the "iron-greening" tannins have 60 per cent. of carbon and 5 per cent. of hydrogen, *e.g.*:

Group I.

	Carbon. Per cent	Hydrogen. Per cent
Gallotannic acid	52.10	3.52
Chestnut wood tannin	52.11	4.40
Chestnut bark tannin	52.42	4.07
Chestnut tannin (*Nass*). . . .	52.07	3.97
Sumach tannin (*Lowe*)	52.42	3.56

Group II.

	Carbon Per cent.	Hydrogen. Per cent.
Oak-bark tannin (av. of 9) . . .	50.79	5.08
Kino tannin (*Bergholz*) . . .	50.65	4.87
Oak-bark tannin (*Etti*)	50.25	4.99
Catechu tannin (*Lowe*)	60.03	4.80
Tormentilla tannin (*Rembold*) . . .	60.75	4.65

The tannins in Group I. give a white precipitate, changing to blue with lime water, whilst in the case of the tannins in Group II., the colour of the precipitate is light pink, changing to red or brown. Bromine water precipitates the tannins in the second group, but not those of the first group.

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* *The Tannins*, ii. p. 132

Suitability of Tannins for Ink-making.—Only the "iron-blueing" tannins are suitable substances for the manufacture of black ink, as has been shown by *Schluttig* and *Neumann*,* who found that mixtures of extracts of pine, catechu, quebracho, kino, and hemlock with solutions of iron salts gave bright green colorations on paper, but after six months' exposure only rust-like stains were left.

Good black inks can be prepared from algarobilla, dividivi, myrobalans, valonia, and sumach, all of which contain "iron-blueing" tannins.

Oak-bark tannin, although an "iron-greening" tannin, also contains a substance giving a blue precipitate with iron salts, and can therefore be used in the manufacture of ink (*vide infra*).

The most important of the tannins suitable for ink are described individually in the following pages.

CHESTNUT BARK AND WOOD.

The Spanish, or Sweet Chestnut (*Castanea vesca*), is a large tree, frequently 80 feet or more in height, which grows abundantly in the countries surrounding the Mediterranean, and in sheltered districts as far north as Scotland. In America it is common in many of the States as far west as Indiana. The fruit is the well-known chestnut, which is largely imported into this country.

Chestnut Extract.—An aqueous extract of chestnut wood or bark is prepared extensively in Pennsylvania and Virginia, the decoctions being subsequently evaporated to a solid mass. According to *Trimble*,† it is impossible to manufacture a good extract without the use of a vacuum pan. It is said to be frequently adulterated with molasses or glucose, and is itself employed to adulterate oak bark extract.

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* *Die Eisengallustinten*, p. 38.

† *The Tannins*, ii. p. 129.

Chestnut Tannin.—*Sheldon*,* who appears to have been the first to call attention to the value of chestnut wood as a tanning and dyeing material, asserted that it contained twice as much tannin as oak bark.

Trimble (*loc. cit.*) found air-dried chips to contain 7.85 per cent. of tannin, which is slightly higher than the amount found by *Sheldon*; whilst *Simand*† found 8.5 per cent. in chestnut wood, and 23.52 per cent. in chestnut-wood extract of 31° Bé., the determinations being made by *Löwenthal's* permanganate method.

Nass‡ was the first to prepare a tannin from chestnut wood, and to determine its composition and properties. The aqueous extract of the wood was fractionally precipitated with sodium chloride, and the final fractions dialysed and then extracted with acetic ether.

In this way he obtained a white preparation which was soluble in water, alcohol, ether, and glycerin, and gave the following reactions when tested in a one per cent. solution.

Reagents.	Chestnut tannin	Gallotannic acid
Ferrous salt . .	No change.	No change.
Ferric ammonium sulphate . . .	Blue-black precipitate.	Blue-black precipitate.
Tartar emetic and ammonium chloride . .	Slight precipitate.	Slight precipitate
Bromine water .	No precipitate.	No precipitate.
Lime water . .	Light precipitate, becoming light blue.	White precipitate, becoming light blue
Sulphuric acid (1 : 10) .	No deposit on boiling.	No deposit on boiling.

When heated to 200° C. it was converted into pyrogallic and metagallic acids, and gave an acetyl derivative closely resembling that of gallotannic acid.

Its elementary composition was also found to be very similar to that of gallotannic acid, as is shown by the following results obtained by *Nass* and by *Trimble*§:

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* *Amer. Journ. Science*, 1819, i. 313.

† *Dingler's polyt. Journ.* 1885, cclv. 487.

‡ *Zeit. anal. Chem.*, 1886, xxv. 134; also Trimble, *The Tannins*, ii. p. 124

§ *loc. cit.*, p. 127.

	Chestnut tannin (*Nass*)	Chestnut wood tannin (*Trimble*).	Chestnut bark tannin (*Trimble*)	Gallotannic acid.
	Per cent	Per cent	Per cent.	Per cent
Carbon . .	52.20	52.42	52.11	52.17
Hydrogen .	3.97	4.67	4.40	3.10

In *Trimble's* opinion this similarity in composition and reactions renders it highly probable that chestnut tannin is identical with the gallotannic acid from galls.

Ink from Chestnut Wood.—*Sheldon* (*loc. cit.*) in 1819 found that chestnut wood contained [illegible] as much substance giving a black coloration with iron (*i.e.*, tannin), as was present in logwood (hæmatoxylin). He stated that it was probably unequalled as a material for ink, since it gave a rich blue-black colour with iron, whilst galls or sumach used in the same proportion had a redder shade. The ink formed by chestnut decoction was blue, but on paper it dried, yielding an intense black. The permanency of the ink was tested by exposing the writing to the sun and air, and was found highly satisfactory.

Schluttig and *Neumann*,* however, in their comparative tests on the stability of inks prepared from different tannin materials, found that chestnut iron-ink, originally blue-black, was fainter than the ink from most of the other "iron-blueing" tannins (p. 50).

In 1825 *Giroud* took out a patent (Eng. Pat. No. 5285) for a substitute for galls, to which he gave the name of "damajavag." This was prepared by soaking 1 cwt. of the wood of the chestnut tree, or shells of the nut, with water for twelve hours, and then boiling it with 180 to 200 quarts of water and evaporating the decoction to a paste, which was to be used in the manufacture of ink, or in tanning.

An ink prepared by us from chestnut extract had a good blue-black colour. On standing exposed to the air for a month it yielded a deposit containing 7.37 per cent. of iron.

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* *loc. cit.* p. 38.

SUMACH.

Sumach or *Sumac* is the name given to the leaves of various plants belonging to the natural order *Rhus*.

Of these the Sicilian sumach, *Rhus coriaria*, grows wild in Spain, Portugal, and other Mediterranean districts, and is also widely cultivated in these countries. The most esteemed variety of Sicilian sumach, known as *Alcamo*,

Fig 23.—Sumach (*Coriaria myrtifolia*).

occurs in commerce as a light green powder with an aromatic odour. A second and inferior variety, which is chiefly used in dyeing, has a more yellow shade and contains less tannin

The best French sumach is very similar to that grown in Sicily. Another French variety, known as *redon*, is obtained from *Coriaria myrtifolia* (Fig 23)

In preparing sumach for the market, the branches are dried in the sun, and the leaves removed and ground to powder in mills.

The leaves of the Venetian sumach, *Rhus cotinus*, a shrub cultivated in Italy and the south of France, contains a yellow dyestuff, and a tannin which gives an olive-green compound with iron salts, and is therefore unsuitable for ink-making.

In America two species of *Rhus*, *R. copallina* and *R. glabra*, both of which contain much less tannin than Sicilian sumach, are extensively used as tanning materials.

Sumach Tannin. —The proportion of tannin in sumach varies considerably, but the usual limits are from about 13 to 20 per cent.

Stenhouse[*] was the first to show the similarity in composition and properties between the tannin of sumach and gallotannic acid, both yielding gallic acid and pyrogallol. The percentage composition of his sumach tannin was: Carbon, 49.73 to 50.12; hydrogen, 3.64 to 3·76; and oxygen, 46.24 to 46.51.

Lowe[†] obtained a purer product by extracting Sicilian sumach with alcohol, treating the residue from the extract with water, extracting the tannin by means of acetic acid, and purifying it by repeatedly dissolving it in water, and precipitating it with sodium chloride. Gallic acid (which was not identified) would be left in solution in the sodium chloride treatment.

Lowe confirmed *Stenhouse's* statement of the formation of gallic acid from the tannin. Crystals of the latter were obtained by heating the tannin solution either alone or with 2 per cent. of sulphuric acid for several hours in a sealed tube placed in a brine bath.

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[*] *Mem. Chem. Soc.*, 1842, i. 135.

[†] *Zeit. anal. Chem.*, 1873, xii. 128.

The properties of the Sicilian sumach tannin were found to be identical with gallotannic acid, and analysis showed them to have the same composition, corresponding with the formula $C_{14}H_{10}O_9$.

Löwe was doubtful whether the tannin of other species of sumach could also be regarded as identical with gallotannic acid. Thus a tannin prepared from Tyrol sumach contained 52.3 per cent. of carbon and 3.8 per cent. of hydrogen, corresponding with the formula $C_{16}H_{14}O_{10}$. Moreover, this tannin differed from that of Sicilian sumach in not yielding gallic acid when heated in a sealed tube with sulphuric acid.

Sumach contains a small quantity of a yellow dyestuff, *quercetin*.

Ink from Sumach.—As the tannin of sumach is identical, or at least allied to that of galls, it was to be anticipated that it would yield an ink of a very similar character, only modified slightly by the colouring matter of the leaves. In fact, *Ribaucourt* * found that the ink made from it had a greenish shade.

Lewis,† who made experiments in 1763 with sumach as an ink material, came to the conclusion that it was inferior to galls as a source of tannin.

Schluttig and *Neumann*,‡ however, have shown that sumach iron-ink is but little inferior in durability to ink prepared from Chinese galls, and superior to "Knoppern" ink. According to *Viedt*,§ ink is occasionally prepared from sumach on a manufacturing scale.

Divi-divi.

Divi-divi is the name given in commerce to the dried pods of the South American shrub, *Cæsalpinia coriaria* (Fig. 24), which was not known in Europe until the latter half of the eighteenth century. It grows in low-lying marshy lands, attaining a height of twenty to thirty feet.

The pods are of a dark brown colour, and about one and a half to three inches in length. They have a very astrin-

* *Ann. de Chim.*, 1792. xv. 156.

† *loc. cit.* p. 382.

‡ *loc. cit.* p. 38.

§ *Dingler's polyt. Journ.*, 1875. ccxvi. 453.

gent taste, due to the tannin, which is for the most part concentrated in the rind immediately beneath the epidermis. The recorded amount of tannin ranges from 30 to 52 per cent. A commercial sample examined by us contained 36 per cent.

Divi-divi Tannin.—*Stenhouse* * separated a tannin from divi-divi, which he found to have the following composition: Carbon, 50.12; hydrogen, 3.72: and oxygen, 4.62.

This tannin yielded gallic acid and pyrogallol, and formed deep blue insoluble compounds with ferric salts, and was thus very similar in composition and properties to gallotannic acid.

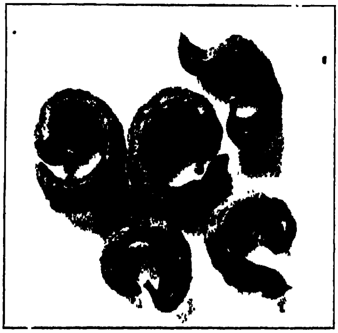

Fig. 24.—Divi-divi pods.

In a more extended research, *Löwe* † found that the tannin of divi-divi behaved with most reagents like gallotannic acid, from which it was distinguished, however, by yielding a deposit of ellagic acid when heated in aqueous solution in a sealed tube.

He therefore described this tannin as ellagitannic acid, and ascribed to it the formula $C_{14}H_{10}O_{10}$, which may be regarded as gallic acid, $C_{14}H_{12}O_{10}$, minus 2 atoms of hydrogen, or gallotannic acid, $C_{14}H_{10}O_9$, plus 1 atom of oxygen.

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* *Mem. Chem. Soc.*, 1842, i. [illegible].

† *Zeit. anal. Chem.*, 1875, xiv. 35.

Lowe also found the same tannic acid in myrobalans.

A specimen of divi-divi examined by us contained 34 per cent. of tannin, determined colorimetrically, and expressed in terms of gallotannic acid.

Ink from Divi-divi.—*Stenhouse (loc. cit.)* states that calico printers had attempted to use divi-divi as a substitute for galls, but had not found it satisfactory, owing to the large proportion of other extractive matters (gums).

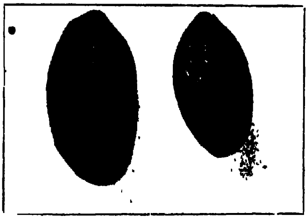

Fig. 25.—Myrobalans

In the case of ink this would not be so objectionable, and in fact *Viedt*[*] asserts that divi-divi is sometimes used in Germany as a source of ink-tannin.

An ink was prepared by us from an extract of divi-divi (5 grms.), treated with 1 grm. of ferrous sulphate. The deposits yielded by this ink contained from 6.77 to 7.77 per cent. of iron.

MYROBALANS.

The dried fruit of different species of *Terminalia* growing in India and the East Indies is sold as a tanning and dyeing material under the name of myrobalans (Fig. 25).

The ripe fruit weighs between 5 to 10 grms., and has a very astringent taste, due to the tannin in the husk.

[*] *Dingler's polyt. Journ.*, 1875, ccxvi. 453.

The Indian species, *T. chebula*, which yields the "black" or "chebulic" myrobalans of commerce, is extensively used in conjunction with iron salts as a black dye, and is also employed in the manufacture of ink.

The earliest mention of the possible use of myrobalans as a substitute for galls is that made by *A. Johnson*[*] in a communication to the Society of Arts in 1801, in which he stated that the natives in India used them to give a black colour to leather, mixing the powder with iron filings and water.

A committee of the Society appointed to report on the subject found that the pulp and outer husk of the fruit gave a rich black colour with ferrous sulphate.

Ink prepared by us from myrobalans was of a good blue black colour, and yielded insoluble deposits containing about 6 per cent. of iron.

The Tannin of Myrobalans.—*Löwe*[†] found about 1 per cent. of gallic acid in myrobalans, and extracted a tannin which contained 49.42 per cent. of carbon and 3.16 per cent. of hydrogen, corresponding with the formula $C_{14}H_{10}O_{10}$.

When heated in a sealed tube at 108-110° C., a solution of this tannin yielded a deposit of ellagic acid; and from this fact and the elementary analysis, *Löwe* concluded that it was ellagitannic acid, identical with that of divi-divi.

Zölffel[‡] confirmed *Löwe*'s statement of the occurrence of 1 per cent. of gallic acid, but found that the tannin was a mixture of ellagitannic acid, and a glucoside of gallotannic acid, the former being in the greater proportion.

A specimen of myrobalans examined by us was found to contain 39 per cent. of tannin determined colorimetrically, and expressed in terms of gallotannic acid.

VALONIA.

Valonia is the commercial name for the acorn cups of certain species of oaks growing in Asia Minor and different parts of Greece, of which the most important are *Q. ægilops* and *Q. macrolepis*.

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[*] *Trans. Soc. Arts*, 1801, xix. 343.
[†] *Zeit. anal. Chem.*, 1875, xiv. 35.
[‡] *Arch. der Pharm.*, 1891, ccxxix. 155.

The best sorts are gathered before the fruit is quite ripe in April, those beaten from the trees in September and October being poorer in tannin.

The cups (containing the acorns) are first partially dried on the ground and then conveyed by mules to Smyrna, where they are stored in warehouses until slight fermentation sets in and causes the acorns to fall from the cups.

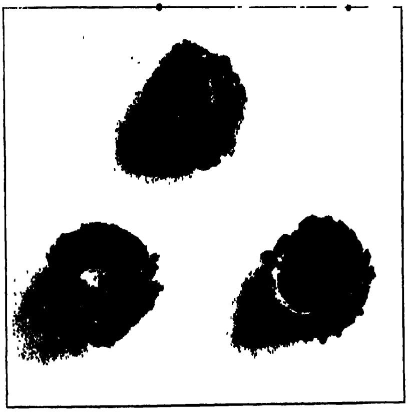

Fig. 20.—Valonia

If exposed to rain after gathering, the acorn cups turn black and lose a considerable amount of tannin by fermentation.

As met with in commerce valonia consists of semicircular prickly backed cups, about 50 mm. in diameter (see Fig. 20).

The amount of tannin they contain varies greatly with the district, species of oak and time of collection, but usually ranges from about 20 to 45 per cent.

The following percentages have been recorded *inter alia*: 32.4 (*Handtke*); 38 (*Galloer*); 22.6-39.2 (*Rothe*); and 31.6 to 35.64 (*Simand*).

*Eitner** examined eighteen samples of different origin of the harvest of 1886, and found them to yield from 42.4 to 51.9 per cent. of total extract. 1.6 to 3 per cent. of soluble ash, and 21.28 to 30.2 per cent. of tannins.

The best valonia is that obtained from Smyrna, the Greek and Albanian products being held in much smaller esteem.

In 1852 the prices per cwt. were as follows: Smyrna, 14s. to 15s.; Morea, 10s. to 12s.; and Camata, 14s. to 16s. (*Tomlinson*). The prices given by *Procter* in 1885 were considerably higher, viz., Smyrna, 12s. *6d.* to 20s. *6d.*; Morea, 10s. *6d.* to 18s. *6d.*; and Camata, 15s. to 19s. per cwt.

The Tannin of Valonia.—This appears to be mainly ellagitannic acid, judging by the results of *Böttinger*,† who extracted the tannins from valonia, divi-divi, and algarobilla, and prepared the acetyl derivative of each The amount of acetyl in the valonia tannin (44.1 per cent.) was nearly the same as that of divi-divi (43.19 per cent.) and algarobilla (43.9 per cent.), and hence *Böttinger* concluded that the preparations were identical in composition.

In the colorimetric estimation of the amount of tannin in terms of gallotannic acid we found the solution yielded a much bluer tinge than the standard solution of gallotannic acid, and it was necessary to add a slight trace of an aniline colour to the latter, in order to match the tint. In duplicate determinations we found (1) 59.1 per cent. and (2) 57.5 per cent. The amount found by *Procter's* hide powder method was 20 per cent., so that the tannin in valonia appears to have a greater tinctorial value than gallotannic acid. The filtrate from the hide powder contained iron-colouring substances (gallic acid), corresponding to 2.5 per cent. of gallotannic acid.

Ink from Valonia.—Valonia yields a very rich bluish black ink, and appears to us to be a very suitable raw material for the manufacture, especially if used in admixture with Chinese galls.

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* *Der Gerber*, 1887, xiii. 18.

† *Ber. d. d. chem. Ges.*, 1884, xvii. 1503.

The deposits yielded by the ink on exposure to the air are very similar to those given by gall or divi-divi inks. Thus the deposits examined by us contained from 11.5 to 12.8 per cent. of iron oxide.

OAK-BARK TANNINS.

Owing to the fact that infusions of oak bark give a blue coloration with iron salts the tannins present were formerly regarded as identical with gallotannic acid. This error was first pointed out by *Stenhouse*,* who showed that an infusion of oak bark differed from a solution of gallotannic acid in not yielding gallic acid or pyrogallol.

In 1867 *Grabowski* found that instead of gallic acid an amorphous red compound, "oak red," was produced, which *Etti*† obtained by boiling an oak tannin with dilute sulphuric acid, and concluded to be an anhydride with the formula $2C_{17}H_{16}O_9 - H_2O = C_{34}H_{30}O_{17}$.

An extended series of researches on the oak tannins were then made independently by *Etti*, by *Lowe*, and by *Bottinger*, but the most conflicting results were obtained. Thus *Etti* prepared an oak tannin which did not dissolve in water and gave a green coloration with ferric salts, whilst *Lowe* obtained soluble tannins with the formulæ $C_{28}H_{28}O_{14}$ and $C_{28}H_{30}O_{15}$, which gave blue precipitates with iron solutions.

Trimble‡ has given an excellent summary of these different results, though without succeeding in reconciling them. He himself has made numerous preparations, and has found the average composition of nine of these to be as follows: Carbon, 59.79; hydrogen, 5.08; and oxygen, 35.13 per cent.—results which correspond best with the formula of *Etti's* tannin, $C_{20}H_{20}O_9$.

In *Trimble's* opinion there is no question but that oak tannins give green colorations with iron salts, and he attributes the blue colorations given by oak-bark infusions to the presence of an associated colouring-matter. In the case of the chestnut oak he separated this "iron-blueing" compound by first precipitating the oak tannins with neutral lead acetate and then treating the filtrate with basic lead acetate.

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* *Mem. Chem. Soc.*, 1842, i. 140.

† *Monatsh. f. Chem.*, 1880, i. 262.

‡ *The Tannins*, ii. p. 10.

Reactions of Oak Tannins.—On heating oak-bark tannins to 190° C. catechol is formed as the main decomposition product, whilst on fusion with caustic alkali protocatechuic acid is obtained.

The colour reactions vary greatly with the species of oak whence the tannins were derived, which is evidence that they are not identical.

*Trimble** gives the following table of the reactions of the tannins separated from two species of oak bark compared with those given by gallotannic acid:

Reagent	English oak, *Q. robur.*	Indian oak *Q. sessiliflora.*	Gallotannic acid
Copper sulphate.	Precipitate.		No precipitate
Copper sulphate ammonia.	Red brown precipitate.	—	Brown precipitate
Stannous chloride and HCl.	Violet colour.	Violet colour	Slight green colour.
Sodium sulphite.	Pink colour.	Yellow colour	Slight pink colour.
Bromine water	Yellow precipitate.	Yellow precipitate.	No precipitate
Ferric chloride.	Blue green colour and green precipitate.	Green colour and precipitate	Blue colour and precipitate.
Ferric chloride + ammonia.	Purple brown precipitate.	Purple brown precipitate.	Purple precipitate
Ferric ammonium sulphate.	Blue green colour and green precipitate.	Green colour and precipitate.	Blue colour and precipitate.
Lime water.	Precipitate turning pink.	Precipitate turning pink	Precipitate turning blue.

Amount of Tannins in Oak Bark.—*Procter* gives the proportion of tannins in European oak bark as 10 to 12 per cent, whilst *Trimble** found the bark of different species of American oaks to contain from 4.04 to 14.21 per cent., whilst an English oak bark gave 12.37 per cent. calculated on the dry substance.

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* *loc. cit.* ii. p. 48

The chief species of oak from which the commercial bark is derived are *Q. pedunculata*, *sessiliflora*, and *pubescens*, the first of which usually contains more tannin than the others.

*Eitner** has shown that the amount of tannin varies with the season. Thus in the case of the bark from *Q. pedunculata* he obtained the following results: April, 14.80; May, 10.71; June, 12.33; July, 9.8; and August, 11.23 per cent.

W[illegible]† analysed commercial oak barks of different origin with the following results:

Origin	Tannin Per cent.		Ash Per cent.	
Hungarian (3)	10.5[illegible]	13.47	5.08	7.31
German (3)	11.87	16.18	6.27	8.52
French (3)	13.8[illegible]	16.22	6.11	7.77
English (3)	13.80	16.23	6.06	7.81
Swedish	12.02	14.50	5.55	7.05
Average	13.50		6.82	

Ink from Oak Bark.—*Stenhouse* (*loc. cit.*) found that a good blue-black ink could be prepared from an infusion of oak bark, in which respect it differed from the infusions of kino, larch, and alder barks, which only gave green colorations with iron salts.

According to *Prechtl*,‡ oak bark was used fifty years ago in conjunction with other substances in the manufacture of ink. Thus he gives the following formula for the preparation of ink from oak-bark galls and *Knoppern*: Galls, 9 lbs., logwood 1½lbs., rasped oak bark, 8lbs., Knoppern 6lbs., gum 3lbs., ammonium chloride ½lb., infused in 40 quarts of water and 24 quarts of vinegar, and the infusion mixed with ferrous sulphate.

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* *Der Gerber*, iv. 85.

† *Ibid.* 1885, ii, 181.

‡ *Technol. Encyclop.*, 1852, xviii. 460.

Since the pure oak tannins are "iron-greening" substances, whilst the blue-black colour given by oak-bark infusions with iron salts is only due to the presence of an associated substance (*oak sepia*), the use of oak bark for ink is not economical. Moreover, ink prepared exclusively from the infusion has been shown by *Schluttig* and *Neumann*[*] to be somewhat less stable on exposure to light and air than the inks from galls, divi-divi, or other substances containing "iron-blueing" tannins.

GALLOTANNIC ACID.

The tannin which is best known is that contained in galls, and to this the name of *gallotannic acid* has been given to distinguish it from *quercitannic acid* and other tannins. It is present in Aleppo, Chinese and Japanese galls and in *Knoppern*, and has also been identified in sumach, myrobalans, and algarobilla.

Pelouze[†] prepared gallotannic acid by extracting powdered gall with ether containing water, and showed that on exposure to the air in an aqueous solution it gradually yielded an insoluble deposit consisting mainly of gallic acid.

Strecker[‡] came to the conclusion that gallotannic acid was a glucoside, which was decomposed on fermentation in accordance with the equation

$$\underset{\text{Glucoside}}{C_{34}H_{28}O_{22}} \quad \underset{\text{Glucose.}}{C_6H_{12}O_6} \quad \underset{\text{Tannic acid.}}{2C_{14}H_{10}O_9} \quad H_2O$$

Subsequently it was shown by *Schiff*[§] that perfectly pure gallotannic acid was free from glucose, and was an anhydride containing two gallic acid groups, *i.e.*, digallic anhydride. In his opinion the glucose in *Strecker's* preparation was originally present in the galls, and had been extracted simultaneously with the tannic acid.

Trimble[‖] concludes that although gallotannic acid can be so purified as to be eventually only digallic anhydride, it is rarely if ever met with in that state in the "pure" article of commerce, which contains variable amounts of glucose in a loose state of combination. In his opinion the commercial article must be regarded either as a glucoside of digallic acid, or as a mixture of the glucoside and of the pure anhydride.

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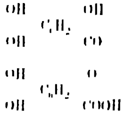
[*] *Die Eisengallustinten*, p. 38.
[†] *Ann. Chem. Pharm.*, 1833, lv. 337.
[‡] *Ibid.* 1854, xc. 238.
[§] *Ibid.* 1873, clxvii. 43.
[‖] *The Tannins*, i. p. 29.

Schiff (*loc. cit.*) prepared a pentacetyl derivative of gallotannic acid, which melted at 137° C., and had a composition agreeing with the formula $C_{14}H_5(C_2H_3O)_5O_9$.

This compound was insoluble in water and cold alcohol, and gave no coloration with iron salts.

The following constitutional formula represents the formation of this acetyl derivative, and also the formation of gallic acid by the hydration of the gallotannic acid:



$$\begin{array}{ccc} OH & & OH \\ & C_6H_2 & \\ OH & & CO \\ & & \\ OH & & O \\ & C_6H_2 & \\ OH & & COOH \end{array}$$

Fermentation of Gallotannic Acid.—*Chevreul* showed that by keeping a solution of gallotannic acid in a sealed tube so as to exclude atmospheric oxygen, it could be kept unchanged for an indefinite period.

It has frequently been asserted (*e.g.*, by *Viedt*, p. 43), that the conversion of gallotannic acid is due to the action of an oxidising enzyme. It was shown, however, by *van Tieghem*[*] that this was not the case, but that the spontaneous change was due to the action of two mould fungi, *Penicillium glaucum* and *Aspergillus niger* in the presence of air. By inoculating solutions of gallotannic acid with the spores of these fungi, he was able to effect a complete conversion of that substance into gallic acid in a few days. The fermentation only took place within the liquid, for when there was only a surface growth a very small amount of gallic acid had been produced after several days' vigorous fermentation. From the results of *Sacc's*[†] experiments it

[*] *Comptes Rendus*, 1867, lxv. 1091.

[†] *Ibid.* 1871, lxxii. 766.

would seem that ordinary yeast also possesses the hydrolysing property of these two ferments.

Properties of Gallotannic Acid.—Gallotannic acid is a yellowish-white, glistening, amorphous powder, which is readily soluble in water, alcohol, and ether.

When heated with dilute acids (*Stenhouse*) or fermented (*vide supra*) it takes up water and is converted into gallic acid, whilst when boiled with alkaline solutions it yields gallic and ellagic acids. When heated alone to 160° C. it is decomposed and yields a sublimate of pyrogallol (See p. 50).

Gallotannic acid gives dark violet or blue precipitates with iron salts. It is precipitated quantitatively by lead salts, with which it yields white compounds, and it forms white unstable gelatinous precipitates with antimony. It combines with gelatin to form an insoluble compound (leather).

GALLIC ACID

Gallic acid ($C_7H_6O_5 + H_2O$), which was discovered by *Scheele*, is present naturally in small proportion in various vegetable substances, such as tea, galls, and myrobalans (about 1 per cent.).

It is obtained from gallotannic acid by fermentation with certain mould fungi (p. 43), or by the hydrolysing action of dilute acids:

$$C_{14}H_{10}O_9 + H_2O = 2C_7H_6O_5.$$

Its constitutional formula shows that it may be regarded as benzoic acid, in which three atoms of hydrogen are replaced by hydroxyl groups:

$$C_6H_2(OH)_3.COOH + H_2O.$$

Properties.—Gallic acid crystallises in white silken needles, which melt above 200° C. It is much less soluble in water than is gallotannic acid, 1 part requiring 130 parts at 12.5° C. to bring it into solution.

It is more soluble in absolute alcohol, 100 parts of which at 15° C. dissolve 27.95 parts, whilst 100 parts of ether at the same temperature only dissolve 2.5 parts.

When heated alone to about 215° C. it is decomposed with the formation of pyrogallol ($C_6H_3.(OH)_3$) and water.

When heated with sulphuric acid at 100° C. it gives off red vapours of rufigallic acid, whilst under the influence of arsenic acid at a high temperature it yields ellagic acid.

It combines with alkalies to form salts, which, in alkaline solution, absorb oxygen from the air and turn brown.

Ferric salts are reduced by gallic acid with the formation of blue-black compounds containing iron in the ferrous condition (*Chevreul*).

Ferrous sulphate free from ferric salts gives no coloration with gallic acid, but ferric sulphate gives a blue colour and eventually a precipitate (*Wackenroder*).

Unlike tannic acids, gallic acid yields no insoluble compound with gelatin.

Various formulæ for the preparation of ink from gallic acid are given on pp. 66–68.

Reactions distinguishing between Gallotannic and Gallic Acids.—It has been generally accepted that tannic acid gives black *precipitates* with ferric salts, and *no coloration* with ferrous salts, but *Ruoss*† has recently shown that these statements are incorrect. He has found that tannic acid gives a black precipitate with ferric acetate and a black precipitate or coloration with ferrous acetate.

Moreover, he has also proved that on adding a solution of a ferric salt drop by drop to a solution of tannic acid only a dark coloration (and no precipitate) is obtained, the iron tannate being readily soluble in an excess of tannic acid. Since gallic acid behaves in the same way, a dark coloration with ferric salts is inconclusive.

Ruoss has therefore devised the following two new reagents, which he has found to be both characteristic and very sensitive:

Ruoss's Reagent I. (1) solution of 20 grms. of ferric sulphate per litre; (2) solution of 28 grms. of crystalline sodium carbonate per litre; (3) acetic acid (sp. gr. 1.04), containing 5 grms. of sodium tartrate per litre.

The tannin solution is diluted to such an extent that on

Cf. Schluttig and Neumann, *loc. cit.* p. 18.

† *Z. anal. Chem.*, 1902, xli. 725.

adding the ferric sulphate solution drop by drop it still remains slightly transparent when the maximum colour has been reached. About 10 c.c. of such a solution are treated with the iron solution (1), which is added drop by drop until the colour ceases to become darker. The same number of drops of solution (2) are then added, and twice that quantity of solution (3). When the liquid is shaken and allowed to stand a black precipitate is obtained in the case of tannic acid, whilst gallic acid yields no such precipitate.

The reaction is capable of detecting 0.001 per cent. of tannic acid.

Ruoss's Reagent II. (1) a solution of 10 grms. of ferric sulphate + 15 grms. of sodium acetate + 1.7 grms. of sodium tartrate per litre; (2) a solution of 1.25 grms of gelatin in 125 c.c. of hot water, made up to a litre with glacial acetic acid (sp. gr. 1.064).

Ten c.c. of the tannin solution are treated with solution (1), added drop by drop until the colour ceases to darken, and then with the same quantity of solution (2). After being shaken and left for some time a flocculent blue-black precipitate indicates tannic acid.

*Ruoss's Oxidation Reaction.** One drop of the ferric sulphate solution (20 grms. per litre) is added to 10 c.c. of the tannin solution, diluted as required in the test with Reagent I. A permanent dark coloration is obtained with tannic acid, whilst gallic acid gives a black coloration, immediately changing to yellow.

If ferric acetate be used instead of ferric sulphate the dark coloration is permanent with gallic acid as well as with tannic acid.

Griessmayer's Reaction† for tannic acid consists of adding one drop of a solution of tannin to a very dilute solution of iodine. The liquid becomes colourless, and on now adding a drop of a dilute solution of ammonia a blood-red colour is produced.

Ruoss has pointed out that the reaction is also given by gallic acid, and is therefore inconclusive.

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* *Loc. cit.* p. 732.

† Classen, *Handbuch der qual. Anal.*, p. 163.

Hydrogen Peroxide as a Reagent.—It has recently been found by *Mitchell* and *Hepworth* that on adding hydrogen peroxide to a solution containing tannin and ferrous sulphate, there is an immediate black precipitate, the tannin being precipitated quantitatively, or nearly so, as a basic tannate: whereas gallic acid treated in the same way yields a dark-brown solution, but only a slight trace of any insoluble compound. The precipitates yielded on ignition from 30 to 34.5 per cent of ferric oxide, and thus approximated in composition to one of *Ruoss's* basic tannates (p. 70).

We attempted to base a quantitative method of separating tannin on this reaction, but were unable to obtain concordant results

CHAPTER III.

NATURE OF INKS

CONTENTS.—Constitution of ink-forming substances—Influence of light and air—**Iron tannates**—Evidence of an intermediate blue iron oxide—Tannates of iron—Basic salts—**Methods of estimating tannates**—Procter's method—Jean's alkaline carbonate method—Hinsdale's ferric sulphate method—Colorimetric methods—Hinsdale's colorimetric method—Mitchell's colorimetric method.

Constitution of Ink-forming Substances. The property possessed by gallic and tannic acids of forming blue compounds with ferric salts has been attributed by *Schiff*[1] to the presence of free phenoloid hydroxyl groups, to which is also due the analogous colorations obtained with other compounds of the aromatic series.

Thus, when a coloration is obtained with ferric chloride the presence of a free hydroxyl group may be inferred, and *vice versa*.

For instance, a *violet* coloration is given by phenol, salicylic acid, phenyl-sulphonic acid, &c.; a *blue* coloration by gallotannic acid, gallic acid, pyrogallol, arbutin, and many derivatives of tannic acid; a *green* colour by many tannins, aesculetin, and paraesculetin; a *red* or *violet-violet* colour by phloridzin, tyrosin, &c.; whilst no coloration is obtained with picric acid, dinitro-hydroquinone, acetylgallic acid, &c.

Schiff also came to the conclusion that the intensity of the colour stood in relation to the number of free hydroxyl groups, the substances giving *violet* colorations containing only one free hydroxyl, whilst deep *bluish-black* colorations were produced by compounds containing several free hydroxyl groups. Thus, phenyl-sulphonic

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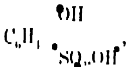
[1] *Ann. Chem. Pharm.*, 1875, clx., 164.

acid,  $C_6H_4\left\{\begin{array}{l}OH\\SO_2.OH\end{array}\right.$, gives a violet colour, whilst gallic acid, $C_6H_2(OH)_3COOH$, gives a blue-black colour.

Schiff's work was extended in a special direction by *Kostanecki*,* who investigated the relation between the constitution of certain organic dyestuffs and their tinctorial properties. He found that phenoloid colouring matters combine with oxide mordants when they possess two hydroxyl groups in the ortho position.

In a subsequent communication, *Kostanecki* † gave the name of "tinctogen group" to that atomic grouping which enables dyestuffs to combine with oxide mordants.

The further question of the formation of permanent "inks" upon vegetable fibres was thoroughly studied by *Schluttig* and *Neumann*.‡

In order to determine whether any phenol compound giving an intense coloration with iron salts was suitable for ink, they made a series of tests in which each substance was dissolved in water (with a little alcohol if required), and then treated with the same proportion of a solution of ferrous sulphate.

The liquids were allowed to run down white paper stretched at an angle of 45°, so as to form stripes 3 to 6 mm. in breadth as in their "Stripe test" (p. 121), which were then allowed to dry.

In the case of phenol, resorcin, hydroquinone, phloroglucinol, orcin, triacetylgallic acid, trimethyl-pyrogallol, and some other compounds, nothing but a faint yellow stain due to iron oxide was obtained.

On the other hand, dark violet colorations of varying intensity were given by gallic and tannic acids, pyrogallol-carboxylic acid, methyl and ethyl esters of gallic acid, potassium pyrogallol-sulphonate, and haematoxylin.

From these and similar experiments *Schluttig* and *Neumann* established the fact that in order to yield colours forming a permanent ink on paper, the compound must contain three hydroxyl groups in juxtaposition. For instance, hydroquinone $C_6H_4\begin{matrix}OH\\OH\end{matrix}$ does not yield an ink, whilst haematoxylin and gallic acid, each of which contains three adjacent hydroxyls,

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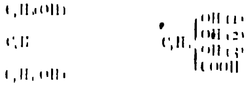
* *Ber. d. d. chem. Ges.*, 1887, xx. 3146.

† *Ibid.*, 1888, 3113, foot-note.

‡ *Die Eisengallustinten*, p. 10.



$C_6H_3(OH)_2$ [illegible] $C_6H_2(OH)_3$

Haematoxylin.

$C_6H_2\begin{cases}OH\ (1)\\OH\ (2)\\OH\ (3)\\COOH\end{cases}$

Gallic acid.

give permanent colorations.

The colour produced by the other substances were as resistant to the action of water and in some cases (*e.g.* esters of gallic acid and haematoxylin) more resistant than the ordinary inks of gallic and tannic acids.

Influence of Light and Air.—On exposing stains given by the different compounds that formed inks for six weeks to the action of a current of air and bright sunlight, the following results were observed:

Completely bleached.—Colours of paroxybenzoic acid and ortho-carboxylic acid.

Yellowish grey.—Pyrogallol-sulphonic acid, tribrompyrogallol, dibrom-gallic acid, and tannic acid.

Dark grey.—Monobrom-gallic acid, pyrogallol-carboxylic acid, and gallic acid.

Dark brown.—Pyrogallol.

Greenish, or Bluish-black.—Pyrocatechin, protocatechuic acid, methyl and ethyl esters of gallic acid, and haematoxylin.

From these results it appears that the inks of tannic and gallic acids are not the most permanent, but are far exceeded in this respect by logwood (haematoxylin) and other inks.

The behaviour of tannic acid ink was remarkable, for it was the faintest of the colorations in its group: whereas if the accepted formula, in which there are five hydroxyl groups, of which three at least are adjacent (see p. 67), be correct, it should have been one of the darkest.

The stability of the inks was found to stand in proportion to their darkness on exposure.

Schluttig and *Neumann* consider that these experiments show conclusively that a determination of gallic or tannic acid in an ink (as prescribed by a German statute, p. 14), without reference to the presence of other compounds of the same character, is of no value as a test of the permanency of that ink.

It has recently been shown by one of us (*Mitchell*)[1] that this law of atomic grouping, established by *Schluttig* and *Neumann*, in the case of iron inks also applies to inks containing ammonium vanadate in place of iron.

IRON TANNATES.

Compounds of Iron and Tannic Acid. Numerous metallic compounds of tannic acid have been prepared, but the iron salts are of primary importance in the manufacture of ink. Although nickel, cobalt and manganese are so closely allied to iron, it is remarkable that none of them forms an "ink" with tannic acid.

On adding a ferrous salt to tannic acid no coloration is at first produced, though under the influence of the atmospheric oxygen the liquid speedily becomes violet, then darkens into an ink, and eventually deposits a violet-black compound (*vide infra*). On the other hand, when a ferric salt is added to a solution of tannic or gallic acid reduction takes place, and ferrous iron can be detected in the liquid (*Chevreul*).

Evidence of an Intermediate Blue Iron Oxide.—*Berzelius* concluded that in these changes a new acid of blue colour was produced, but *Barreswil*[2] showed that the evidence pointed to the presence of compounds of tannic or gallic acid with an intermediate blue oxide of iron.

Thus, on mixing ferrous and ferric sulphate, and immediately placing the mixture in sulphuric acid to eliminate water, a deep blue mass is obtained. An evanescent blue sulphate is also produced by evaporating a solution of the two sulphates nearly to dryness. Similarly by using crystalline sodium phosphate instead of sulphuric acid a deep blue iron phosphate is obtained. *Barreswil* was unable to isolate this blue oxide, but since the purest blue colorations were obtained with sulphuric acid, gallic acid, and sodium phosphate, when the mixture contained three equivalents of ferrous salt to two equivalents of ferric salt, he inferred that the hypothetical blue oxide had the composition Fe_5O_7, or $3FeO . 2Fe_2O_3$.

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[1] *Analyst*, 1903, xxviii. 146.

[2] *Comptes Rendus*, 1843, xvii. 739.

Tannates of Iron.—In 1833 *Pelouze*[*] studied the nature of the compound formed on adding *ferric* sulphate to a solution of tannin. The precipitate, when washed and dried at 120° C., yielded 12.0 per cent. of ferric oxide (= 8.4 per cent. of iron).

Wittstein[†] prepared a series of insoluble compounds of some of which there is reason to doubt the individuality.

1. On leaving a solution containing $1\frac{1}{2}$ parts of tannin and one part of *ferrous* sulphate exposed to the air for a month, a precipitate with 8.40 per cent. of ferric oxide was obtained. This is apparently the substance formed when ink dries on paper (*Hepworth* and *Mitchell, infra*).

2. From a solution containing three parts of tannin to one part of ferric acetate a precipitate yielding 20.15 per cent. of ferric oxide was obtained.

3. On diluting the dark blue solution a resinous precipitate with 13.49 per cent. of ferric oxide resulted.

4. Tannin solution added drop by drop to ferric acetate solution gave a precipitate yielding 50 per cent. of ferric oxide.

5. On adding ferric acetate solution to a tannin solution the precipitate yielded 25 per cent. of iron oxide.

Schiff[‡] pointed out that the series of salts described by *Wittstein* might be grouped into two series, viz., those in which the hydrogen in a molecule of acid might be regarded as being replaced by the monovalent group—$[FeO]$, and those in which several molecules of the acid gradually replaced the hydroxyl groups in ferric hydroxide—$Fe_2(OH)_6$.

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[*] *Ann. de Chim. et Phys.*, 1833, liv. 337.

[†] *Jahresber. der Chem.*, 1848, xxviii. 221.

[‡] *Ann. Chem. Pharm.*, 1875, clxxv. 176.

Schiff's Formulæ for the Iron Tannates of Pelouze and Wittstein.[*]

Formula	Iron calculated Per cent.	Ferric oxide calculated Per cent.	Ferric oxide found Per cent.
$C_{14}H_9(FeO)O_9$	14.21	20.3	20.15
$C_{14}H_7(FeO)_3O_9$	31.30	44.8	Wittstein prepared compounds containing 42.8 to 59.3
$C_{14}H_6(FeO)_4O_9$	36.95	52.8	
$C_{14}H_5(FeO)_5O_9$	41.39	59.0	
$Fe_2(C_{14}H_8O_9)_3$			
$Fe(C_{14}H_9O_9)_3$	5.53	7.9	8.4 (Wittstein)
$C_{14}H_9O_9$ Fe $C_{14}H_9O_9$ $C_{14}H_9O_9$ Fe $C_{14}H_9O_9$	8.0	11.5	12.0 (Pelouze)
$C_{14}H_8O_9$ Fe $C_{14}H_8O_9$ Fe $C_{14}H_8O_9$	10.43	14.9	13.4, 14.9, 15.4 (Wittstein)
O Fe $C_{14}H_8O_9$ $C_{14}H_8O_9$ Fe O	14.21	20.3	20.15 (Wittstein)
HO O – Fe, $C_{14}H_8O_9$ O $C_{14}H_8O_9$ O Fe_2 HO $C_{14}H_9O_9$	17.03	25.2	25.0 (Wittstein)

Schiff considers it doubtful whether some of *Wittstein's* gelatinous deposits were individual compounds, but at the same time points out that the agreement between the theoretical values and the results actually obtained is remarkable.

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[*] See also a formula on p. 89, suggested by Schiff, which corresponds better with the amount of iron found by *Wittstein*, and by *Mitchell* and *Hepworth*.

*Vudt** states that he has prepared an iron tannate consisting of 17.8 grms. of iron to 100 grms. of tannin, but gives no details of the analysis.

Schluttig and *Neumann's* and *Mitchell* and *Hepworth's* experiments on the composition of the spontaneous deposit from a solution of ferrous sulphate and tannic acid are described at length below.

Basic Salts.—Roos† has recently described a basic iron tannate consisting of a previously unknown ferric tannate in combination with ferric hydroxide.

This was prepared by treating a tannin solution with sodium carbonate solution, and adding ferric sulphate solution to the soluble sodium tannate formed. The excess of iron could be removed by treating the basic tannate with normal acetic acid, leaving the insoluble ferric tannate.

This, when dried at 100° to 120° C., contained 15.0 per cent. of iron, as against 14.9 per cent. required by a tannate of the formula—

$$(C_{14}H_7O_9)Fe$$

Taking into consideration the formation of other basic salts, *Roos* subsequently came to the conclusion that it must be regarded as tannin in which the hydrogen of the carboxyl group was replaced by the monovalent group [FeO], thus—

$$C_{14}H_9O_9FeO = C_{14}H_7O_9Fe + H_2O.$$

Similar black basic salts, containing two, three, four, or five atoms of iron in the molecule, were prepared, but when more iron was introduced the colour became brownish-black.

These salts may be regarded either as compounds of the normal tannate $(C_{14}H_7O_9)Fe$, with ferric hydroxide, or as compounds in which the group [FeO] replaces hydrogen, both in the carboxyl group and in the hydroxyl of the ferric hydroxide, *e.g.*—

$$(C_{14}H_7O_9)Fe + 3Fe(OH)_3 = (C_{14}O_9H_6)(FeO)_4 + 5H_2O.$$

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* *Dingler's polyt. Journ.*, 1875, ccxvi. 456.

† *Zeit. anal. Chem.*, 1902, xli. 732.

We give the amount of iron in these basic salts dried at 100° C., so that they may be more readily compared with the compounds of *Wittstein* and other earlier investigators.

Basic Tannates of Rœss.

Formula.	Iron Per cent.	Ferric oxide Per cent.	Iron found Per cent.
$(C_{14}H_7O_9)Fe$	14.9	21.27	15.0
$(C_{14}H_7O_9,2Fe(OH)_3$	22.42	31.88	—
$(C_{14}H_7O_9,3Fe(OH)_3$	31.40	44.85	—
$(C_{14}H_7O_9,4Fe(OH)_3$	36.96	52.70	—
$(C_{14}H_7O_9,6Fe(OH)_3$	41.30	58.90	

Since the composition of these basic salts varies with the concentration of the iron solution used for the precipitation, *Rœss* points out that they may also be regarded as merely mixtures of the normal tannate with ferric hydroxide.

Rœss has based a method of determining tannin upon its precipitation as the tannate $(C_{14}H_7O_9)Fe$ (*vide infra*).

Iron Tannate precipitated by Hydrogen Peroxide.—*Hepworth* and *Mitchell** investigated the nature of the tannate formed on adding hydrogen peroxide to a solution containing tannin and ferrous sulphate. There was an immediate dense black precipitate, which rapidly subsided, leaving a colourless solution. The precipitates thus obtained, when dried at 100 C., were found to contain from 21 to 22.5 per cent. of iron, and were probably basic tannates.

Gallic acid treated in the same manner yielded only a very slight deposit, but the colour of the solution changed to dark reddish-brown.

Attempts to base a quantitative method of determining gallotannic acid on this reaction have so far proved unsuccessful.

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* Unpublished results.

METHODS OF ESTIMATING TANNIN.

The methods of determining tannins are very numerous, and attempts have been made to utilise most of the reactions that seemed likely to give anything approaching quantitative results. Thus precipitation with gelatin and with all kinds of metallic salts have been tried, but the results of different observers have been far from concordant, which must be largely attributed to the fact that there are numerous tannins, and that these vary in their behaviour with different chemical reagents.

For valuation of tannin materials for leather manufacture the methods chiefly used are *Loewenthal's* method which is based on the reduction of potassium permanganate by tannins, and *Procter's* method, which depends on the absorption of the tannin by purified hide powder.

In the permanganate method an aqueous solution of the tannin material is first titrated with potassium permanganate solution with indigo carmine as indicator to obtain a valuation of all the reducing substances present The tannin is then precipitated by means of gelatin, and the filtrate again titrated, the difference between the two results giving the amount of tannin in terms of potassium permanganate. The method will thus give the relative tanning value of two samples of the same kind of material, but numerous precautions are essential: for the speed of titration, strength of the solution, and other factors, have an influence on the results. This method, which does not estimate gallic acid or other compounds (other than tannin) that give a coloration with iron salts, is an unsuitable one for the valuation of tannin material for ink manufacture.

Procter's Method.—We have found *Trimble's*[*] apparatus (Fig. 27) a very simple and satisfactory one for the determination of tannin by *Procter's* method. This consists of a cylinder of about 500 c.c. capacity, and a funnel-shaped tube about 18 cm. in length, and 2.5 cm. in width at the bottom, whilst the other end tapers to a fine tube on which is fixed a piece of flexible rubber tubing to form the other limb of the siphon.

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[*] *The Tannins*, ii. p. 98.

A small piece of cotton wool is pushed lightly down to the narrow end, and the tube then loosely packed with

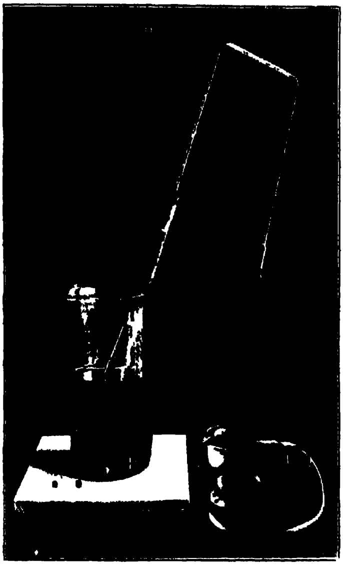

Fig. 27.—Trimble's apparatus for tannin determination.

8 to 10 grms. of purified hide powder, and the opening closed with a large piece of cotton wool.

The tannin infusion is poured into the cylinder a little at a time, so as to gradually moisten the hide powder. After standing for about two hours the liquid is gently siphoned through the indiarubber tube, the first 30 to

40 c.c. being rejected. Fifty c.c. of the filtrate are then evaporated to dryness on the water-bath, the difference between the weight of the residue and that previously obtained by evaporating 50 c.c. of the tannin before the filtration giving the amount of tannin absorbed by the hide.

Trimble obtained results by this method higher than those given by the permanganate and alum gelatin methods.

The method should be employed by the ink manufacturer in conjunction with a colorimetric one.

Jackson's Lead Carbonate Method.[1]—This is based upon *Jackson's* determination that a 1 per cent. aqueous solution of gallotannic acid has a specific gravity of 1003.8 at 15.5 C.

The extract or decoction of the substance is diluted to a litre, and its specific gravity determined at 15.5 C. (*e.g.*, 1003.86). It is then shaken with dry lead carbonate at intervals for two to three hours, after which it is filtered and the specific gravity of the filtrate determined. The loss in specific gravity (*e.g.*, 1003.86−1001.52=2.34) divided by 3.8 and multiplied by 20 gives the percentage of tannin absorbed by the lead (*e.g.*, in this case=12.30 per cent.).

Jackson obtained the following results with solutions of 5 per cent. strength:—

	Specific gravity of solution	Specific gravity of filtrate.	Tannin Per cent.
Valonia .	1009.08	1003.33	30.2
Sumach .	1008.25	1003.61	24.4
„ . . .	1009.61	1005.08	23.8
Oak-wood extract, .	1007.33	1003.15	21.9
Chestnut wood extract	1006.06	1002.48	18.8

The filtrate from the lead precipitate in this method forms a black ink with iron salts, and the method is unsuitable for valuing tannin materials for ink manufacture unless used in conjunction with a colorimetric method.

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[1] *Chem. News*, 1884, l. 1079.

Ruoss's Ferric Sulphate Method.*—This is based upon the formation of sodium tannate and the subsequent precipitation of the tannic acid as the compound $C_{14}H_9O_9$ (FeO) (*vide supra*) by means of a solution of ferric sulphate containing sodium tartrate to prevent spontaneous formation of basic ferric oxide and acetic acid to dissolve the ferric hydroxide, which would otherwise be precipitated simultaneously with the tannic acid.

The reagents required are: (1) a solution of 50 grms. of ferric sulphate (or an equivalent quantity of ferric chloride or ferric ammonium sulphate) per litre; (2) a semi-normal solution of crystalline sodium carbonate (71.3625 grms. per litre); and (3) a solution of 5 grms. of sodium tartrate in a litre of dilute (6 per cent.) acetic acid.

It is essential that the ferric sulphate be at least equivalent to the sodium carbonate solution, *i.e.*, when 10 c.c. of each are boiled together and filtered, the filtrate must not give an alkaline reaction with methyl orange. In preparing it the liquid must not be boiled, or basic iron compounds will be deposited.

A further test to be applied to the solutions is that on mixing 50 c.c. of water, 10 c.c. of solution (1) and 10 c.c. of solution (2), and immediately adding 25 c.c. of solution (3), the liquid must remain perfectly clear after being boiled for five minutes.

The tannin solution may be neutral or faintly acid or alkaline, but must not contain more than 0.4 per cent. of tannic acid.

In the determination 50 c.c. of such a solution are shaken with 10 c.c. of solution (2) and 10 c.c. of reagent (1) (an evolution of carbon dioxide taking place), and then *immediately* mixed with 25 c.c. of the sodium tartrate solution (3), well shaken, and boiled for five minutes. It is then filtered, and the precipitate washed until the washings are free from iron, and then dried, ignited, and weighed.

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* *Zeit. anal. Chem.*, 1902, xli. 717.

The weight of the residue multiplied by the factor

$$\frac{321.22 \cdot 0.7001}{56} = 4.024$$

gives the amount of tannic acid (mol. weight = 321.22) in 50 c.c. of the tannin solution.

Gallic acid treated in the same way gives a brown coloration, but no precipitate with the reagents, and passes into the filtrate, where it might be determined colorimetrically.

This method has not proved satisfactory in our hands as a means of determining the value of tannin material for the manufacture of ink; and although closely following the directions given, we have been unable to obtain concordant results in experiments with solutions of pure gallotannic acid.

Colorimetric Methods.—It is obvious that the ordinary gravimetric methods used by the leather manufacturer for the valuation of tannic materials are not very suitable for the purposes of the ink manufacturer who wishes to take into account all the substances capable of forming coloured compounds with iron salts, and not merely those forming insoluble compounds with gelatin.

The filtrate from the determination of tannin by *Procter's* method almost invariably gives a dark colour with solutions of ferric salts, and this is more marked in the case of samples of old material in which the original gallic acid has undergone more or less decomposition. For instance, we found old English oak-apple galls to contain 11 per cent. of tannin by the gelatin absorption method, whereas the filtrate from the gelatin compound gave a deep blue-black colour with ferric salts, and when tested by our colorimetric method was found to contain substances equivalent in tinctorial effect to an additional 18 to 19 per cent. of gallotannic acid.

Hinsdale's Colorimetric Method.—*Hinsdale* * has described a method in which the reagent was prepared by dissolving 0.04 grm. of potassium ferricyanide in 500 c.c. of water and adding 1.5 c.c. of ferric chloride solution (Amer. Pharm. strength).

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* *Amer. Journ. Pharm.*, 1890, lxii. 149.

The standard tannin solution consisted of 0.04 grm. of pure gallotannic acid dried at 100 C.

In determining the proportion of tannin in, *e.g.*, oak-bark, 0.8 grm. of the sample was exhausted with successive quantities of boiling water, and the extract made up to 500 c.c. Five drops of this extract were then treated with 5 c.c. of the reagent, and the same quantity added to 4, 5, 6, 7, and 8 drops of the standard tannin solution. After one minute 20 c.c. of water were added, and the colours matched within three minutes.

Hinsdale asserts that the method is applicable to any substance containing less than 10 per cent. of tannin. In the case of stronger solutions an equal volume of water must be added and the results multiplied by 2.

We have made a number of determinations by this method, but in our opinion it has the drawbacks of requiring the tannin solution to be so very dilute, whilst the reagent, in addition to being unstable and possessing too dark a colour, gives somewhat indecisive colorations with tannin, which are not easy to match.

We therefore discarded it in favour of the following colorimetric process.

Mitchell's Colorimetric Method.*—The reagent consists of a solution of 0.1 grm. of ferrous sulphate and 0.5 grm. of sodium tartrate in 250 c.c. of water. On adding this to a dilute solution of gallotannic acid or gallic acid a violet coloration is produced, the intensity of which is proportional to the amount of these acids present.

The standard solution for colorimetric comparison consists of 0.1 grm. of dried gallotannic acid in 500 c.c. of water, and the whole of the substances giving a coloration with the reagent are expressed in terms of gallotannic acid.

Gallic acid may also be used for the standard solution, and the results expressed in terms of that acid.

The colorimetrical comparison may be suitably made in the tubes first designed by *Hehner* for Nesslerising water. These are placed on a white tile, and the colour of the liquid in each matched. The amount of gallotannic acid in the tube containing the standard solution being known, the equivalent amount in the other tube can then be readily calculated.

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* Unpublished.

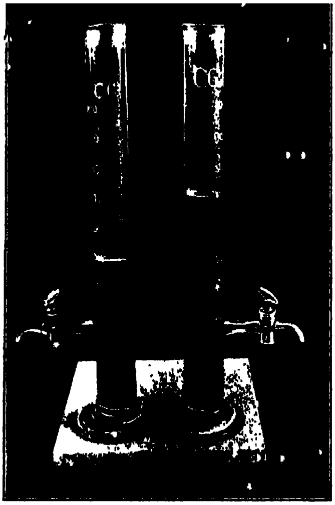

Fig. 28.—Hehner's Nesslerising tubes.

In this way the following results were obtained:

Nut galls, 44 per cent.; oak-apple galls, 30.7 per cent.; divi-divi, 34 per cent.; valonia, 57.5 and 59 per cent.; myrobalans, 39 per cent.; Japanese galls, 56 per cent.; and Chinese galls, 62 per cent.

CHAPTER IV.

MANUFACTURE OF IRON GALL INK.

CONTENTS.—The relative proportion of galls and ferrous sulphate—Deductions from the composition of ink deposits—**Old type of iron gall ink**—Old formulæ of iron gall inks—**Unoxidised iron gall inks—Gallic acid inks—Japan inks.**

THE process of preparing ink from Chinese or Aleppo galls is a very simple one. The galls are crushed, mixed with straw, and treated with hot (not boiling) water in a high narrow oak vat containing a false bottom. The liquid percolates through small holes in this, its passage being assisted by the presence of the straw, and is then drawn off through a cock and pumped over the goods again and again until the whole of the tannin has been extracted.

The final extract, which should contain from 5 to 6 per cent. of tannin (*Viedt*), is then mixed with a solution containing the necessary amount of ferrous sulphate.

THE RELATIVE PROPORTION OF GALLS AND FERROUS SULPHATE.

Historical Opinions.—If we compare the numerous formulæ given by different chemists who have investigated the subject, it will be observed that there is frequently a great discrepancy of opinion.

One of the earliest published formulæ is that given in 1660 by *Canneparius*,[*] in which 3 parts of galls are to be used to 1 part of ferrous sulphate.

Lewis,[†] who made experiments with varying quantities in 1748, found that equal parts of galls and ferrous sulphate yielded a good black ink, but that the colour faded in a few days to brownish-yellow on exposing the writing to the light. An infusion from 2 parts of galls mixed with 1 part of ferrous sulphate had not faded so much after two months' exposure, whilst with a proportion of 3 to 1 the colour was preserved still better. By still further increasing the proportion of galls to 6 : 1, the writing was paler but more durable. The proportion of water was found to admit of much greater variation, but 40 to 50 parts yielded an ink of sufficient blackness and permanency.

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[*] *De Atramentis.*

[†] *loc. cit.* p. 377.

Ribaucourt[*] confirmed *Lewis's* statement as to the influence of an excess of iron upon the writing, and also showed that when the galls were in excess the characters soon changed to brownish-yellow on exposure.

From his experiments he concluded that a proportion of 2 of galls to 1 of ferrous sulphate was sufficient to make a good ink, and that *Lewis's* proportion of 3 to 1 was too great.

Other proportions recommended are 4 : 1 (*Eisler*,[†] 1770); 5 : 1 (*Reid*[‡]); 1.5 : 1 (*Brande*[§]); 2.4 : 1 (*Ure*[‖]); &c. &c.

All these proportions were obtained, empirically, with galls which probably contained very variable proportions of gallotannic acid, and by methods in which different amounts of that substance were brought into solution. But making allowance for this, the balance of opinion, which is also supported by numerous authorities not quoted above (*Booth*, *Karmarsch*, *Hochheimer*, &c.), is in favour of a proportion of 3 parts or thereabouts of galls to 1 part of ferrous sulphate.

This conclusion is supported by the experiments of *Schluttig* and *Neumann* on the composition of the insoluble iron compound that forms on exposing the solution of gallotannic acid and ferrous sulphate to the action of the air, and by our own experiments on similar lines.

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[*] *Ann. de Chim.*, 1792, xv. 113.

[†] *Loc. cit.*

[‡] *Phil. Mag.*, 1827, ii. 114.

[§] *Dict. of Science*, art. Ink.

[‖] *Dict. of Chem.*

Deductions from the Composition of Ink Deposits.—Of the numerous compounds of tannin and iron, which have already been described (p. 76), that formed during the spontaneous oxidation of the ink is the only one that need be considered here, for the insoluble tannate produced by oxidation with hydrogen peroxide has a completely different composition (*loc. cit., supra*).

Wittstein * exposed a solution of tannin and ferrous sulphate in the proportion of 3 : 1 to the atmosphere for a month and a half, and thus obtained an insoluble precipitate which, when dried at 100° C., yielded 8.40 per cent. of ferric oxide (=5.88 per cent. of iron). He proved that gallic acid was not formed in the oxidation, since the liquid, after repeated treatment with gelatin to remove tannic acid, yielded a filtrate which did not darken on the addition of ferric salts. The precipitate contained $\frac{1}{15}$ of its iron in the ferrous state.

The formula which best corresponds with this proportion of iron is that suggested by *Schiff*,† which requires 8.5 per cent. of iron:

$$\begin{array}{ll} \mathrm{Fe} & (C_{14}H_9O_9), \\ & C_{14}H_8O_9 \\ \mathrm{Fe} & (C_{14}H_9O_9), \end{array}$$

Schluttig and *Neumann*,‡ on repeating *Wittstein's* experiments, obtained a series of five spontaneous precipitates which they removed from the ink from time to time, the final one being collected after an exposure of five weeks. These five precipitates, dried at 100° C., were found to contain from 6.27 to 6.61 per cent. of iron, the average in the five being 6.35 per cent.

Precipitates obtained in the same manner and allowed to dry spontaneously in the air contained on the average 4.8 per cent. of iron. A complete analysis of one of these air-dried deposits gave the following results: Carbon, 35.77; hydrogen, 5.19; iron, 4.80; and oxygen, 54.24 per cent. When these precipitates were dried at 100° C., the dark violet colour changed to black, and they were

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* *Jahresber. der Chem.* (von Berzelius). 1848. xxviii. 221.

† *Ann. Chem. Pharm.*, 1875. clxxv. 176.

‡ *Die Eisengallustinten*, Dresden, 1890. p. 44.

Amount of Iron in Spontaneous Deposits from Inks.

No.	Tannin, &c.	Ferrous sulphate.	Water.	Time before collecting the deposit.	Ferric oxide in deposit.	Iron in deposit.
		Grms.	C.c.			
1	Gallotannic acid (86 %) (2 grms.)	3	100	1 month	8.22	5.75
2	" "	"	"	3 days.	8.49	5.94
1	Gallotannic acid (86 %) (3 grms.)	3	100	1 week	7.85	5.49
2	"	"	"	"	8.63	6.04
1	Gallic acid (3 grms.) (very slight deposit)	2	250	2 months	25	17.5
1	Chinese galls, decoction from 12 grms.	3	200	10 days	9.0	6.3
2	" " "			7 "	10.3	7.2
3		"	"	3 weeks	10.8	7.55
4		"	"	2 "	10.71	7.50
1	Aleppo blue galls, decoction from 5 grms.	1	200	4 days	8.62	6.04
2	"	"		10 "	11.03	7.72
3				3 weeks	10.6	7.4
1	English oak-apple galls, from 5 grms.	1	200	2 weeks	14.8	10.3
2	"	"	"	1 week	12.9	9.0
3	"	"	"	1 "	13.1	9.2
1	Japanese galls (5 grms.)	1	300	6 days	11.31	7.91
2	" " "	"	"	3 weeks	11.02	7.71
3	" " "	"	"	6 days	11.6	8.12
1	Divi-divi (5 grms.)	1	200	2 weeks	9.70	6.77
2	Ink decanted from first sediment	"	"	2 "	11.1	7.77
1	Valonia (5 grms.)	1	200	1 week	11.53	8.1
2	" "	"	"	2 weeks	12.78	8.9
1	Myrobalans (5 grms.)	1	200	2 weeks	8.21	5.74
1	Chestnut extract (5 grms.)	5	200	1 month	10.53	7.37

then found to contain 6.34 per cent. of iron, or the same proportion as the deposits dried directly at that temperature.

The ratio of iron to tannin was thus as 1 : 14.27 (or 1 part of ferrous sulphate to 2.88 parts of tannin)—a result which agreed fairly well with *Dieterich's* empirical proportion of 1 part of iron to 15 parts of tannin.

As there was considerable discrepancy between the composition of the deposits obtained by *Wittstein* and by *Schluttig* and *Neumann* we thought it advisable to once more repeat the work, using not only tannin, but also extracts of different kinds of galls.

Our results, which, as will be seen, were obtained under very varying conditions, are summarised in the preceding table.

Our results with pure gallotannic acid are thus more in agreement with those of *Wittstein* than with those of *Schluttig* and *Neumann*.

It was hardly to be expected that galls should not contain other substances besides gallotannic acid forming insoluble compounds with iron, and this probably accounts for the higher percentage of iron found in the deposits from English oak-apple gall ink, &c.

We found that the precipitates attacked the paper if dried on the filter at 100 C., and we therefore in most of our experiments washed the deposits into a platinum basin, in which they were subsequently dried and ignited.

The ratio between the iron and gallotannic acid in our dried deposits was as 1 : 16, which corresponds with a ratio of 1 : 3.2[illegible] between the ferrous sulphate and gallotannic acid.

Hence each part of ferrous sulphate requires 3 parts of pure gallotannic acid. Since, however, the proportion of tannic acid varies in each kind of material employed, the proportion of tannin material must naturally vary correspondingly.

The following table, giving the approximate proportions of different materials, is based upon the average amount of tannin they contain, and on the results of the preceding experiments. It is assumed that practically the whole of the tannin is extracted in each case.

*Proportion of Tannin Materials required by 1 part of Ferrous Sulphate.**

Tannin material	Containing pure tannic acid	Parts by weight required.
	Per cent (circa)	
Commercial gallotannic acid	80	3.8
Aleppo galls	62	5.0
Chinese galls	75	4.3
Japanese galls	62	5.0
Acorn galls (Knoppern)	30	11
English oak-apple galls	26	12.5
Chestnut wood	9	36
" " extract	20	16
Sumach	22	14.6
Valonia	30	11
Divi-divi	40	8
Myrobalans	30	11

OLD TYPE OF IRON GALL INK.

When solutions of gallotannic acid and ferrous sulphate are mixed the liquid at first remains colourless, and it is only when oxidation takes place that a violet-black solution and eventually a violet-black deposit is formed.

In the older type of iron gall inks it was therefore necessary to expose the liquid to the air for some time to obtain an ink which would give writing of sufficient immediate blackness, although even the writing with the colourless solution of gallotannic acid and ferrous sulphate gradually becomes black when dried. In other words, a "provisional colour" was formed by partial oxidation of the ink, and the insoluble deposit was kept in suspension by the addition of a sufficient quantity of gum arabic.

Ink thus oxidised yielded an immediate black writing, but had the drawback that that portion of the ink in which the oxidation was complete did not penetrate into the fibres of the paper, but was attached to the surface by means of the gum and could be washed off.

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* See also colorimetric results on p. 60.

In a good iron gall ink of the old type it was therefore essential to have only so much of the ink oxidised as to give an immediate black colour, leaving the remainder in an unoxidised state to penetrate into the paper, and form the black insoluble oxidised tannate within the fibres.

On boiling an iron gall ink the oxidation process is accelerated, and there is also some decomposition of the tannate, so that a complete ink should not be boiled.

Provisional Colouring Matters.—The paleness of the writing with unoxidised ink has also been obviated in many inks by the addition of logwood extract (p. 102), or more recently of various aniline colours (p. 13). Such colouring matters as Prussian or Turnbull's blue, ultramarine, or the various blue compounds of copper, are quite unsuitable for the purpose, since they are either too insoluble or react with the tannin and injure the colour of iron tannate. The most suitable and most widely employed substance as a provisional colour is indigo, the presence of which is a characteristic feature of the so-called "*alizarine*" *inks* (*vide infra*).

Old Formulæ of Iron Gall Inks.—The earliest method of preparing iron gall ink that we have discovered is that of the Elizabethan domestic ink, the formula of which is shown in the frontispiece.

Elizabethan Ink.—Rain water (or claret wine or red vinegar), 1 quart; galls, 5 oz.; ferrous sulphate, 4 oz.; gum, 3 oz. After five days' soaking, the extract from the galls was heated just to the boiling-point with the ferrous sulphate (see also the rhyme of *de Beau Chesne*, p. 12).

*Canneparius** (1660).—Galls, 3 oz., macerated in 30 oz. of white wine for six days, and the extract mixed with 1 oz. of ferrous sulphate and 2 oz. of gum arabic, and left for four days.

Lewis† (1760).—Galls, 3 oz.; rasped logwood, 1 oz.; water, 2 to 3 parts; gum, varied at discretion, but about ½ oz. per pint. The ink to be shaken daily for ten to twelve days.

"*Celebrated Black Dresden Ink*" (1770).‡—Galls, 2 lbs.; ferrous sulphate, ½ lb.; gum, 6 oz.; alum, 2 oz.; verdigris, 1 oz.; and salt, 1 oz.; in 2 quarts of vinegar and 2 quarts of rain water. Decanted after two days and shaken daily for eight days.

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* *De Atramentis*, p. 270.

† *loc. cit.* p. 377.

*Eisler** (1770).—Galls, 4 oz.; ferrous sulphate, 2 oz.; gum, 1 oz.; in a quart of rain water.

Ribeaucourt† (1792).—Galls, 2 oz.; ferrous sulphate, 1 oz.; copper sulphate, ½ oz.; gum, 1 oz.; and logwood, 1 oz.; in 24 oz. of water.

Reid‡ (1827).—Galls (1 lb.) extracted twice with 3 pints of boiling water, and the extract (2 quarts) mixed with 3½ oz. of ferrous sulphate and the same quantity of gum.

UNOXIDISED IRON GALL INKS.

The use of indigo as a means of improving the colour of ink was mentioned by *Eisler* in 1770 (*loc. cit.*), and was used in this country by *Stephens*§ in 1836.

In 1856 *Leonhardi*,‖ of Dresden, patented in Hanover an ink consisting of an extract of 42 parts of Aleppo galls and 3 parts of madder in 120 parts of water, mixed with 1½ parts of indigo solution, 5½ parts of ferrous sulphate, and 2 parts of metallic iron, dissolved in crude acetic acid. Subsequently the madder was omitted as superfluous, but the inks still retained the name of "alizarine" ink, although quite free from alizarine. The more suitable name of "*isatin*" inks never met with popular acceptance.

In "alizarine" inks the process of oxidation is prevented as far as possible, thus keeping the liquid free, to a large extent, from insoluble deposit, and giving it much greater power of penetration into the paper. The presence of the indigo makes the writing immediately blue, and it subsequently changes to black as the oxidation of the iron tannate proceeds within the fibres of the paper, the oxidation process being completed in eight days at the most.

The addition of indigo also increases the permanency of the ink, so that the writing offers much more resistance to the action of bleaching agents than ordinary iron gall inks.

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* Eisler. *Tintefass*, p. 7.
† *Ann. de Chim.*, 1792, xv. 113.
‡ *Philos. Mag.*, 1827, ii. 114.
§ *Mechanics' Mag.*, 1836, xxv. 229.
‖ *Dingler's polyt. Journ.*, 1856, cxlii. 141.

Owing to the absence of gum the inks flow more readily from the pen, and are less liable to clog; but, on the other hand, the presence of free acid in considerable proportion causes the pen to be corroded.

Thus we found that an ordinary steel pen left in a typical commercial "alizarine" ink from which air was excluded had lost 5 per cent. in weight after six weeks, whilst the ink itself had become semi-solid.

Indigo blue is soluble in concentrated sulphuric acid, and the solution can be diluted to a great extent without yielding a deposit.

Viedt[*] gives the following method of preparing "alizarine" ink: a 5 to 6 per cent. solution of sulphindigotic acid is treated with sufficient iron to form the necessary amount of ferrous sulphate for the tannin present. The excess of free acid is then nearly neutralised with chalk or marble, leaving only a slight amount to retard atmospheric oxidation of the ink. The clear solution is then decanted from the insoluble calcium sulphate and mixed with a 5 to 6 per cent. decoction of galls, yielding a green solution through the mixture of the yellow gall extract and blue indigo solution.

Inks containing neutral indigo carmine, *i.e.*, the sodium or potassium salt of sulphindigotic acid, yield deposits much more readily than inks containing free sulphuric acid, though the latter also form sediments in time.

Indigo carmine is prepared by dissolving indigo in sulphuric acid, adding alkali, and collecting and washing the precipitate.

Prollius' "Alizarine" Ink, which was recommended by *Bley*[†] as superior to any then sold, was prepared from (1) $1\frac{1}{4}$ lbs. of galls, with sufficient water to yield 5 lbs. of decoction; (2) 4 oz. of indigo powder mixed with $1\frac{1}{2}$ lbs. of fuming sulphuric acid, and allowed to stand for 24 hours; then diluted with 5 lbs. of water, treated with 8 oz. of powdered chalk, and 8 oz. of iron filings, filtered and added to (1).

Dingler's polyt. Journ., 1875, ccxvi. 533.

Ibid. 1857, cxlv. 77.

With the object of reducing the corrosive action of the sulphuric acid in the ferrous sulphate upon steel pens several manufacturers have proposed to ignite ferrous sulphate until a white powder was left. It is difficult to see what advantage such a process can have.

Desormeaux's gall ink[*] and *Haule's non-corrosive ink*[†] were prepared in a similar manner.

GALLIC ACID INKS.

Reid,[‡] in the course of his investigation on gall inks, pointed out that after the conversion of gallotannic acid into gallic acid more than twice as much ink was produced. Thus 448 parts of galls required 144 parts of ferrous sulphate, but after the conversion of the gallotannic acid into gallic acid 336 parts of the iron salt were necessary to obtain an ink of the same intensity.

To effect this conversion in practice, he exposed a decoction of 1lb. of galls to the air for ten days with continual daily shaking, and then added to each quart of the liquid 3½ pints of water, 9 oz. of ferrous sulphate, and 9 oz. of gum.

Dieterich[§] has also recommended inks prepared from gallic acid solutions obtained by the oxidation of gall extracts or tannin solutions.

Oxidised Gall Extracts.—200 parts of powdered Chinese galls are moistened with water and kept in a warm place (20—25 C.) until quite mouldy, the water being renewed daily, so that the galls feel moist but not wet. After eight to ten days the fermentation is complete, and the galls are extracted with successive portions of hot water, and filtered after the addition of some talc, the total amount of extract and washings amounting to 1000 parts.

Oxidised Tannin Solutions.—100 parts of tannin, 100 parts of water, and 20 parts of hydrochloric acid (sp. gr. 1.16) are heated for ten hours on the water bath at 80—90 C., and then gradually diluted with 900 parts of distilled water.

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[*] *Nicholson's Dict. of Chem*, 1820, p. 507.

[†] Prechtl's *Technol. Encyclop.*, 1852, p. 460.

[‡] *Philosoph. Mag.*, 1827, ii. 111.

[§] *Pharm. Manual*, 1897, p 680.

For writing inks *Dieterich* finds that either ferrous or ferric salts can be used with such oxidised solutions, but for copying inks only ferrous salts can be employed (see chap. xii.). He gives the following directions for preparing inks on these lines:

I. *Gall Ink.*—1000 parts of the oxidised gall decoction are mixed with 100 of ferric chloride solution containing 10 per cent. of iron, the ink left for two weeks in closed flasks and then decanted.

II. *Oxidised Tannin Office Ink.*—100 parts of tannin, 100 of water, 200 of ferric chloride solution (10 per cent. of iron), and 10 per cent. of crude hydrochloric acid (sp. gr. 1.16) are mixed and heated for ten hours at 80—90 C. The liquid is then diluted with 700 parts of hot water, left for an hour at the same temperature (with renewal of the evaporated water), cooled, kept in a closed flask for two weeks, filtered, and diluted to 1000 parts.

With inks thus prepared the writing is at first hardly perceptible, so that a provisional colour is necessary, as in the case of the following formulæ:

Blue-black Iron Gall Ink.—Three parts of phenol blue in 400 parts of water are mixed with 600 parts of oxidised gall ink (I.) and 1 part of phenol, and left for a week in a loosely covered flask, after which the clear ink is decanted.

Violet-black Ink.—Prepared in the same way, except that 1.5 parts of phenol blue 3 F., and 2.0 parts of Ponceau red R.R. are used, instead of the 3 parts of phenol blue as the provisional colour.

Red-black Ink.—Six parts of Ponceau red R. used.

Green-black Ink.—Six parts of aniline green used.

Black Ink.—The provisional colour consists of 10.5 parts of aniline green D, 9 parts of Ponceau red R, and 1 part of phenol blue 3 F.

"*Alizarine*" *Ink.*—Four parts of indigotin, and 2.4 parts of aniline green as colouring matter.

Blue-green Ink.—1.5 parts of phenol blue, and 2.5 parts of aniline green as colouring matter.

For the formulæ of gallic acid copying inks on these lines see chap. xii.

State of Massachusetts Official Ink.—This is a mixed tannic and gallic acid ink, containing the following constituents:—Dry gallotannic acid, 23.4; gallic acid crystals, 7.7; ferrous sulphate, 30; gum arabic, 25; dilute hydrochloric acid, 25; and phenol, 1, in 1000 parts of water.

JAPAN INKS.

When an iron gall ink has been oxidised so as to have become converted for the most part into the insoluble black iron tannate (p. 13), it no longer possesses the penetrating properties of the freshly prepared ink, and requires the addition of a considerable amount of gum to keep the insoluble powder in suspension.

Such ink gives an immediate black writing, which dries on the surface of the paper with a varnish-like gloss, whence this sort of ink was termed *Japan ink* by *Ribeaucourt.*

Since the oxidation has taken place within the ink instead of partially within the fibres, as in the old type of partially oxidised gall inks, Japan inks are more easily removed than other gall inks. They have also the drawback of stickiness and of the excess of gum clogging the pen, whilst they also readily yield large deposits.

Ribeaucourt's Japan Ink contained the ingredients given in the formula on p. 94. In *Newton's* English patent (No. 836; 1865), complete iron gall ink was oxidised by being percolated through narrow openings in the bottom of a vessel; whilst *Carter* (Eng. Pat., No. 1983; 1873) obtained the same results by subjecting the ink to the action of a current of air.

Both of these processes produce "Japan" inks of the very opposite type to "alizarine" inks.

CHAPTER V.

LOGWOOD, VANADIUM AND ANILINE BLACK INKS.

CONTENTS.—**Logwood inks**—Logwood—Logwood extract—Hæmatoxylin—Hæmatein—Iso-hæmatein—Addition of logwood to gall inks—Logwood inks without tannin—Chrome logwood inks—Hæmatein inks—Use of logwood in patent inks—**Vanadium inks**—**Black aniline inks.**

LOGWOOD INKS.

Logwood.—This well-known dyeing material consists of chips of the wood of *Hæmatoxylon Campechianum*, a large tree (40 to 50 feet high) belonging to the *Cæsalpiniaceæ*. It forms large woods on the Atlantic side of Central America, in Mexico, and in the West Indies.

It was first discovered by the Spaniards in the Bay of Campeachy, in Mexico, and exported by them into Europe. When introduced into England in the reign of Queen Elizabeth, it was soon employed to adulterate other dyes, and its use was prohibited as "affording a false and deceitful colour" injurious to the Queen's subjects, "and discreditable beyond seas to our merchants and dyers." This Act was not repealed until 1661.

The constant hostilities between the Spanish and English led to the tree being acclimatised in the West Indies in 1715, though subsequently a treaty was concluded giving the English the right of cutting and exporting the wood from Campeachy.

The best Indian logwood is not so valuable as the Mexican product, whilst Honduras wood is intermediate in value.

In preparing it for the market, the wood is first divided into logs about 3 feet in length, which are then cut into chips by means of a revolving drum provided with steel cutting knives.

Logwood Extract.—Formerly the chips were moistened and exposed to a fermentation process, but manufacturers now endeavour to exclude all oxidising influences.

Three methods are in use in the preparation of the logwood extracts of commerce.* The finely divided chips are frequently digested with hot water under a pressure of 1 to 2 atmospheres, this process yielding a large extract, which, however, contains a considerable proportion of resins, fats, and other impurities; (2) the French method of boiling the chips with water at the ordinary pressure, which yields a smaller though purer extract; and (3) a diffusion process, in which an apparatus similar to that used in the sugar industry is employed. The yield by this process is smaller than in (1) or (2), but the shades of colour are finer.

If the wood has not undergone any fermentation, the extracts contain chiefly hæmatoxylin and but little hæmatein. They are sold either as liquids, with a density of about 10 Bé., or as solid gum-like masses.

The tinctorial value of an extract is usually determined by practical dyeing tests, the amount of colour fixed on wool mordanted with potassium bichromate and tartaric acid on treatment with a definite quantity of the dried sample, being compared with that given by a sample of standard quality.

Logwood extract may be adulterated with molasses or tannin materials, though according to *Rupe* (*loc. cit.*) adulteration is not so frequent now as formerly.

Hæmatoxylin [$C_{16}H_{14}O_6$].—The colouring matter of logwood does not occur ready formed in the cells, but in the form of a compound, *hæmatoxylin*, which becomes purple on oxidation.

Hæmatoxylin was first discovered by *Chevreul* † in 1810, and termed *hæmatin* by him, a name subsequently changed to *hæmatoxylin* by *Erdmann*, ‡ in order to prevent confusion with the colouring matter of blood.

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* Rupe, *Die Chem. der natur. Farbstoffe*, p. 107.

† *Ann. Chim. Phys.*, 1812, lxxxii. 53, 126.

‡ *Ann. Chem. Pharm.*, 1842, xliv. 292

It was obtained by *Hesse*[*] in the form of colourless crystals containing 3 molecules of water [which they lost at 120 C.], by extraction with ether containing some water and in the presence of alkali bisulphate.

Properties.—Hæmatoxylin has a sweet taste and is slightly soluble in water, but dissolves readily in alcohol and ether. The crystals turn red on exposure to the light (in the absence of air) without changing in composition.

Solutions of silver and gold salts are rapidly reduced by them, as is also the case with Fehling's solution. Stannous chloride gives a rose-coloured precipitate, ferrous ammonium sulphate a slight violet black precipitate, and lead acetate a white precipitate changing to blue.

On dry distillation hæmatoxylin yields pyrogallol and resorcinol (or a derivative).

From a consideration of the results obtained on acetylation *Reim*[†] concluded that hæmatoxylin had the constitutional formula—

$$\begin{array}{l} C_6H_3(OH)_2 \\ | \\ C_6H_4 \\ | \\ C_6H_2(OH)_3 \end{array}$$

Hæmatein ($C_{16}H_{12}O_6$).—The colouring principle of logwood, which is first formed by the oxidation of the preexisting hæmatoxylin, was discovered by *O. Erdmann* (*loc. cit.*)—$C_{16}H_{14}O_6 + O = C_{16}H_{12}O_6 + H_2$.

It forms small anhydrous yellowish-green crystals with a metallic lustre. These are only slightly soluble in water, alcohol or ether, though the solution in water (0.06 per cent. at 20 C.) has an intense colour.

It is readily soluble in alkalies yielding violet or purplish brown compounds. The ammonium compound, $C_{16}H_{12}O_6.2NH_3$ is precipitated by most metallic salts. Thus it yields a violet blue precipitate with copper sulphate, a dark violet with alum, and a black one with iron ammonium sulphate, whilst it reduces a solution of silver nitrate (*Hesse*).[‡]

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[*] *Ann. Chem. Pharm.*, 1859, cix. 332.

[†] *Ber. d. d. chem. Ges.*, iv. 329.

[‡] *loc. cit.*

Hæmatein is reduced to hæmatoxylin by treatment with sulphur dioxide or hydrogen.

Iso-hæmatein.—When hæmatein is treated with concentrated sulphuric acid, it dissolves, forming a brown solution, from which, on standing, a crystalline compound, $\left.\begin{matrix}C_{16}H_{11}O_5\\H\end{matrix}\right\}SO_4$, is deposited (*Hummel and Perkin*).*

If hydrochloric acid be heated with hæmatein in a sealed tube the colour of the solution changes to dirty yellow, and on evaporating the liquid a crystalline deposit of iso-hæmatein hydrochloride is left. By treating this with silver hydroxide, and concentrating the solution *in vacuo*, *iso-hæmatein* is left as an amorphous mass with a greenish metallic lustre.

Iso-hæmatein has the same composition as hæmatein, which it also resembles in its general reactions, though many of the metallic compounds have a more reddish shade of purple.

Addition of Logwood to Gall Inks.—The advantage of adding a small proportion of logwood decoction or extract to iron gall inks has long been known. In 1763 *Lewis*† made a series of experiments to determine whether such an addition had any injurious effect upon the stability of the ink, and found that the colour of the ink was materially improved without lessening its permanency.

He recommended an ink consisting of 3 parts of galls, 1 of ferrous sulphate, and 1 of logwood in 40 to 60 parts of water, with gum arabic in the proportion of ½ part to 20 of ink.

Eisler's Logwood Gall Ink‡ was prepared from the following ingredients:—Logwood, 8 oz.; ferrous sulphate, 8 oz.; vinegar, ½ quart; rain water, ½ quart; galls, 4 oz.; gum arabic, 4 oz; alum, 2 oz.; and indigo, 1 oz. The ink was left for fourteen days in the sun before using.

Ribeaucourt § in 1792 agreed with *Lewis's* statement as to the advantage of logwood in iron gall ink, and recommended that its proportion should be half that of the galls.

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* *Ber. d. d. chem. Ges.*, xv. 2337.

† *loc. cit.* p. 377.

‡ *Dintefass*, 1770, p. 8.

§ *Ann. de Chim.*, 1792, xv. 113.

These earlier results have been fully confirmed in our time by the experiments of *Schluttig* and *Neumann*,* who found that ink prepared from hæmatoxylin and iron was even more permanent than those prepared from gallotannic or gallic acids.

Reid's Gallic Acid Logwood Ink.—*Reid*† found that when gallic acid was employed in place of gallotannic acid logwood might be added in the proportion of 1½ parts to 1 part of the former.

He prepared an ink on these lines by exposing a decoction of galls (1 lb.), to the air for ten days with occasional daily agitation, so as to convert the gallotannic acid into gallic acid, and then adding a decoction of logwood (1½ lbs.), 18 oz. of ferrous sulphate, and 18 oz. of gum.

This ink is decomposed by alkalies and alkali carbonates, the iron being precipitated.

Logwood Inks without Tannin.—Since hæmatoxylin, the active agent in logwood, contains three adjacent hydroxyl groups it follows the general rule established by *Schluttig* and *Neumann* of yielding an ink with iron salts.

The iron logwood inks have a greenish shade, which gradually changes to black as the writing dries. Alum logwood inks have a deep violet-black colour, and chromium logwood inks a violet colour changing to black. Chromic acid added to logwood gives a deep black precipitate, whilst potassium chromate yields a black ink, and if added in excess a black precipitate.

In fact, as *Viedt*‡ has shown, precipitates are gradually formed by oxidation in logwood inks containing alum or iron or copper salts, though more slowly than in iron tannin ink. The addition of logwood in excess does not prevent this, but the deposition is retarded for a long time by completely excluding the air.

Reinige's Iron Logwood Ink.§—This may be taken as a typical ink of this class. It is prepared by dissolving 2 grms. of logwood extract, and 3 grms. of ferrous sulphate, in 100 c.c. of water, then, adding 10 grms. of crystalline sodium carbonate, and finally, 2 grms. of oxalic acid. After complete settlement the ink is decanted from the sediment, and a suitable proportion of gum added.

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* *Die Eisengallustinten*, p. 33

† *Philos. Mag.*, 1827, ii. 115.

‡ *Dingler's polyt. Journ.*, 1875, ccxvi. 456.

§ *Ibid.* 1857, cxliii. 240.

This ink gives a good black writing, but we have found that the characters become somewhat brown after two or three months.

The writing gives a red coloration with hydrochloric and other acids, due to the logwood, and a bluish-green with acidified potassium ferrocyanide solution indicating the iron. It is gradually bleached by bromine water.

Reid,* who investigated the character of the inks formed on adding ferrous sulphate to logwood, found that the greenish-blue compound first formed was gradually oxidised to a brownish-black compound. Copious deposits were given, however, by such logwood iron inks, and hence *Reid* concluded that logwood should not be employed alone, or should not exceed a third of the amount of the galls in mixed inks.

Bottger's Alum Copper Logwood Ink.†—This is prepared by boiling 1 part of alum, 2 of copper sulphate, and 4 of logwood extract with 48 parts of water, and filtering the solution. The filtrate is a red-violet ink, which writes pale violet, but rapidly darkens and soon becomes jet black.

On treatment with bromine water the writing is changed to red, and then to faint brownish yellow.

The great drawback of the ink is its instability, and it must be kept in tightly corked bottles, which should contain as little air as possible. Ink prepared by us and kept in a corked bottle containing air had yielded a dense deposit in six weeks, and gave only faint writing.

Violet-Black Rouen Ink (Encre bleu rouennaise).‡—This consists of a decoction of 75 parts of logwood in 600 parts of water, to which is added $3\frac{1}{2}$ parts of alum, 3 parts of gum arabic, and 1½ parts of sugar candy. The ink is allowed to stand for two or three days and then strained.

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* *Philos. Mag.*, 1827, ii. 114.

† *Dingler's polyt. Journ.* 1857, cxliii. 240.

‡ *Ibid.* 1859, cliii. 77.

Inks containing only logwood and alum write with a reddish-violet colour, which gradually changes to a dark, though not absolutely black, shade.

Viedt's Copper Logwood Ink.[*]—In *Viedt's* opinion copper sulphate should always be used in preference to ferrous sulphate in logwood ink, since it gives a blacker writing.

He recommends the following formula:—Logwood extract, 20 kilos. in 200 kilos. of water, mixed with a solution of 10 kilos. of ammonium alum in 20 kilos. of boiling water, and the mixture treated with 0.2 of sulphuric acid and 1.5 of copper sulphate in 20 litres of water.

In order to obtain a darker liquid the ink is exposed to the air for some days before being bottled, thus producing a "provisional colouring," similar to that given by indigo in "alizarine" inks. Inks of this type are sold under different names, *e.g.*, *Chemnitz violet-black ink*.

To obviate the paleness of the writing given by such inks as this *Stark* has prepared a writing and copying ink which gives immediate black characters by adding a little chromate to a copper logwood ink, the chrome ink in this case representing the "provisional colouring" matter (*cf.* p. 13).

Viedt (*loc. cit.*) states that he has never known an ink of this kind to gelatinise.

A great objection to all logwood copper inks is that they cannot be used with steel pens, which gradually withdraws the copper from them.

The addition of free sulphuric acid, as in *Viedt's* copper logwood ink (*supra*), retards the formation of a deposit, but causes the ink to corrode steel pens.

Chrome Logwood Inks.—*Runge*[†] discovered that by adding a very small proportion of potassium chromate to a decoction of logwood a deep black fluid was obtained, which could be used at once as a writing ink, though by increasing the amount of chromate a black precipitate was produced.

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[*] *Dingler's polyt. Journ.*, 1875, ccxvii. 76.

[†] *Grundriss der Chem.*, 1847, ii. 205; *Dingler's polyt. Journ.*, 1848, cix. 225.

Runge's Chrome Ink.—This was originally prepared by boiling 10 lbs. of logwood with water until 80 lbs. of decoction were obtained, and adding potassium chromate in the proportion of 1 part in 1000.

If solid extract of logwood be used, 15 parts are dissolved in 1000 parts of water, and 1 part of potassium chromate added.

Runge claimed for this ink the advantage of yielding permanent black writing, and of not acting upon steel pens.

Gopel[*] considered that *Runge's* formula had too large a proportion of logwood, as shown by the red-brown edges of drops of the ink on white blotting paper, and advocated the following proportions: logwood extract 24, potassium chromate 2, and water 1000 parts.

In the proportion recommended by *Karmarsch* (1 of chromate to 8 of logwood extract), the ink is too grey, pointing to an excess of the chromate.

Although *Runge* had been able to use his ink continuously for two years, it has been found by others that after a time a coagulation due to some unknown cause may occur.

Stein[†] made numerous experiments to find a remedy for this, and eventually found that the addition of 4 grains of mercuric chloride to a bottle liquefied the coagulated ink and prevented it from becoming thick again.

Viedt,[‡] however, asserts that *Stein's* remedy is useless, and that a better remedy is the addition of sodium carbonate, as in *Bottger's* writing and copying ink (*infra*). He found that such ink, when kept in a well-closed inkstand, remained fluid for two years, and hence concluded that the best means of preserving the ink was to completely exclude the air.

Bottger's Modification of Runge's Ink.[§]—Fifteen parts of logwood extract are dissolved in 900 parts of boiling water, and 4 parts of crystalline sodium carbonate dissolved in the clear decanted solution; a solution of 1 part of potassium chromate in 100 parts of water is finally added.

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[*] *Dingler's polyt. Journ.*, 1859, cli. 80.
[†] *Ibid.* 1850, cxv. 77.
[‡] *Ibid.* 1875, ccvii. 76.
[§] *Ibid.* 1859, cli. 431 : 1869, cxci. 175.

We have prepared ink by each of the above methods. *Runge's* original formula gives an ink which yields very black characters, but requires the pen to be frequently filled, or the writing appears faint. The ink kept in a test-tube closed with cotton wool was perfectly liquid after three months, though it then yielded writing with a browner tinge.

A simultaneous experiment in which a drop of formalin had been added to the ink gave analogous results.

Ink prepared at the same time by *Bottger's* modification, and kept in a large well-closed flask (containing air), had a slight mould on the surface and gave dirty brown writing. Hence the addition of phenol or other preservative is essential for this ink.

According to *Viedt*, *Plaster's* "*Chrome Ink Powder*" and *Poncelet's* "*Ink without Acid*," are imitations of *Runge's* original chrome ink.

A "blue black ink," consisting of logwood decoction and chrome alum, gives writing which is too pale and grey.

Bichromate Logwood Ink.[*]—One hundred parts of logwood extract are dissolved in 800 parts of lime water, and when solution is complete, 3 parts of phenol and 25 parts of hydrochloric acid are introduced, and the whole left for thirty minutes on the hot-water bath. It is then cooled and filtered, 30 parts of gum arabic, and 3 parts of potassium chromate added, and the ink diluted to make 1800 parts.

This ink is violet-red in colour, and the writing at first appears reddish-brown, but rapidly darkens, and within five minutes has a bluish-black tint. It keeps well and yields very little deposit, but, owing to the amount of free hydrochloric acid present, it has a considerable action upon steel pens. Thus in one of our experiments a pen left in the ink had lost 4.5 per cent. in weight after six weeks, whilst the ink itself had become semi-solid.

[*] *Dingler's polyt. Journ.*, 1882, ccxlv. 475.

The basic chloride and acetate of chromium are sometimes used instead of potassium chromate in chrome inks in order to lessen the tendency to gelatinise.

Dieterich's School Ink.—*Dieterich*[*] recommends the following as a cheap and effective ink for school purposes: 200 parts of a 20 per cent. solution of logwood extract are diluted with 500 parts of water and heated to 90 C. A solution of 2 parts of potassium bichromate, 50 of chrome alum and 10 of oxalic acid in 150 parts of water, is then added, drop by drop, and the mixture maintained at 90 C. for thirty minutes, and then diluted to 1000 parts and mixed with 1 part of phenol. After standing for two or three days it is decanted, and is then ready for use.

Hæmatein Inks.—Inks prepared with hæmatein in place of logwood extract have more brilliant shades, but are wanting in lustre, and are readily decomposed on heating.

An alkaline hæmatein ink is prepared by mixing 12 parts of hæmatein with 720 parts of water for two hours at about 20 C., and then decanting the liquid, heating it to 30 C., and adding 3 parts of crystalline sodium carbonate. When cold, 0.5 part of potassium chromate in 48 parts of water is gradually added with constant stirring, and lastly 12 parts of gum and 0.5 part of phenol, with sufficient water to make 960 parts of ink in all.

Schmieder's Acid Hæmatein Ink consists of 24 parts of hæmatein dissolved in water (760 parts) at a temperature not exceeding 39 C., then acidified with 80 drops of strong sulphuric acid, mixed with a solution of 4 parts of ferrous sulphate in 48 parts of water, 12 parts of hydrochloric acid, and diluted to 960 parts, a sufficient quantity of gum being subsequently added.

This ink is dark red in colour, and gives dark red writing, which changes to brown and then to black within twelve hours.

For other formulæ of logwood inks see *Copying Inks*, chap. xii.

Use of Logwood in Patent Inks.—Logwood frequently occurs as an ingredient of patented inks. Thus it is used in *Whitfield's Indelible Safety Ink* (Eng. Pat. No. 7474; 1837), whilst *Scott* (Eng. Pat. No. 8770; 1840) prepared a similar indelible ink, consisting of a logwood iron ink with the adding of gum, indigo, Prussian blue, gas-black and iron nitrate.

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[*] *Pharm. Manual*, 1897, p. 685

In *J. Reade's* patent (Eng. Pat. No. 11,474; 1846), the precipitate obtained by adding metallic salts (iron, copper, potassium bichromate) to logwood extract is incorporated with a printing ink.

In 1856 (Eng. Pat. 342), *C. and G. Swann* claimed an ink prepared by adding potassium bichromate with a sufficient quantity of potassium bicarbonate, potassium chlorate, mercuric chloride and ammonia to a decoction of logwood.

Underwood (Eng. Pat. No. 1112; 1857) patented a logwood copying paper (see chap. xii.), whilst logwood and hæmatoxylin ink powders were claimed by *Cooley* (Eng, Pat. No. 106: 1867), *Byford* (Eng. Pat. No. 974; 1876). and *Grunwald* (Eng. Pat. No. 963; 1881).

Joly (Eng. Pat. No 4484; 1875) prepared an ink by the action of tungstic acid upon colouring matters, such as those of logwood, elderberries, &c.

Fonseca and Co. (Eng. Pat. No. 859; 1883) used logwood as an ingredient of an indelible carbon ink; and *Frusher* (Eng. Pat. No. 8241; 1885) has patented the manufacture of ink from waste logwood and potassium bichromate from dyeing processes.

VANADIUM INKS.

The discovery of the fact that ammonium vanadate forms a black ink with gallotannic acid is attributed to *Berzelius*,* but we have been unable to discover any reference to the subject either in the *Jahresberichte* or *Lehrbuch* of *Berzelius*. The statement that this ink is of a very permanent character has been copied from one text-book to another, and is still found in different standard works on chemistry.

In 1889 *Appelbaum* † made a number of experiments with inks thus prepared from gall extracts and solutions of pure gallotannic acid, and found that both the ink itself and the writing faded after the lapse of a few weeks. Hence he doubted whether *Berzelius* had ever made any experiments with the ink.

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* *Dingler's polyt. Journ.*, 1835, lvi. 237.

† *Ibid.* 1889, cclxxi. 423.

We have repeated the work of *Appelbaum* * and can confirm what he says about gall vanadium inks, though we find that gallotannic acid gives an ink of somewhat greater permanency than was found to be the case by him.

It has been shown by one of us (M.) that the law established by *Schluttig* and *Neumann* (p. 73), for iron salts also applies to ammonium vanadate—*i.e.*, that it yields black ink with substances containing three adjacent hydroxyl groups. Thus gallic acid, logwood extract, hæmatoxylin and pyrogallol combine with ammonium metavanadate to form black inks, whilst phenol, benzoic acid, saccharin, &c., do not form such compounds.

None of these inks, however, have proved satisfactory in our hands. Although they give an immediate black writing, the characters gradually turn yellow, even when protected from the light. Hence, apart from the question of expense, ammonium vanadate cannot be regarded as a suitable constituent of writing inks.

It has, however, been claimed as an addition to inks in various patents. Thus *Pinkney* (Eng. Pat., No. 2745, of 1871) prepares an ink from an aniline salt with a salt of vanadium or uranium and an oxidising agent; and a similar patent was taken out by *Grawitz* (Eng. Pat., No. 1620; 1875). The use of vanadium is claimed by *Hickisson* as a constituent of a marking ink (Eng. Pat., No. 5122; 1878), whilst it is also used by *Just*, *Weiler*, and *Heidepriem* in their patent safety ink (Eng. Pat., 16,757; 1890).

Mitchell (*loc. cit.*) has described certain reactions of vanadium enabling vanadates to be readily distinguished from chromates, which are frequently very similar in colour.

Analyst, 1903, xxviii. 146.

BLACK ANILINE INKS.

The formation of aniline black in a fine state of division within the fibres of the paper was described by *Jacobsen* as an indelible ink for writing or marking, though it has chiefly been used for the latter purpose.

Various brands of nigrosine, which are the sodium salts of the sulphonic acids of anilidophenyl- anilidodiphenyl and dianilidodiphenylsafranin-hydrochloride, are used in the preparation of a black writing ink. They are readily soluble in water, and when dissolved in the proportion of about 1 part in 80 yield a solution which flows readily, dries to a good black, and has no action on metallic pens, The solution keeps well, and the writing resists the action of different chemical reagents, although it can be removed or smudged by water, and lacks the permanency of good iron gall ink.

Coupier and Collins' "Indulin ink,"[*] which was awarded a prize in Paris, was a blue-black ink which, according to *Viedt*, contained nigrosine or similar aniline dye-stuffs.

Solutions of nigrosine were sold under the name of "stylographic ink" when first manufactured in 1867, owing to the readiness with which they flowed from stylographic pens.

Particulars of other aniline inks are given under *Coloured Inks* in chap. vi.

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[*] *Dingler's polyt. Journ.*, 1867, clxxxiii. 78.

CHAPTER VI.

COLOURED WRITING INKS.

CONTENTS.—Historical—**Coloured aniline inks**—Fugitiveness of aniline inks—Patented coloured inks.

Historical.—One of the earliest references to the use of a coloured ink is by *Plutarch*, who mentions a red ink (*πυρρον βαμμα*) with which certain letters were marked on the doors of the *dikasts* in Athens. Red ink compounded with minium or vermilion seems to have been used for the titles of books among the Romans,* whilst *Sidonius* (vii. 12) states that rubrica (red ochre) was used for the same purpose. It is interesting to note that our word "rubric," which is applied to the titles of subsections printed in red, thus finds its origin.

A reddish-purple ink was prepared by the Romans from the *Murex*, the mollusc which yielded the famous Tyrian dye. *Montfaucon* was of opinion that this was the source of the ink used by the Byzantine Emperors in their signatures to documents. In fact, the use of any red ink was forbidden to any one excepting those of royal blood.†

If the Emperor was still a minor, his guardians signed for him in green ink, the general use of which was probably also interdicted to some extent. According to *Astle*,‡ ink of this colour was frequently used in Latin manuscripts, though rarely found in charters; but his remarks apply to later ages.

The same authority stated that blue and yellow ink seldom occurred in old manuscripts, and that he knew of no instance of the latter being used later than 1200 A.D.

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* *Ovid*, *Trist.*, I. i. 7.

† *Cod. Justin.* I. [23].

‡ *Origin of Writing*, 1803, p. 209.

Gold and silver inks were used by both Greek and Roman Emperors at later periods. These probably consisted of the finely divided metals incorporated with some adhesive medium, such as gum. Metallic writing of this character was sometimes burnished or coated with wax.

Wecker (*De Secretis*, 1582) gives details of the composition of ink of different colours, and refers to gold and silver inks.

In the work of *Canneparius* (1660), to which we have frequently referred, various formulæ for coloured inks appear, such as solution of verdigris in vinegar for green ink, &c.

The use of both indigo and logwood as dye-stuffs was forbidden in England in the reign of Elizabeth, and the Act was not repealed until the reign of Charles II. (*vide supra*). After that they gradually came into use as constituents of writing inks, and are now widely employed in the manufacture of black writing inks.

Inks can be made of any desired tint, for a variety of pigments and dye-stuffs are at the manufacturers' disposal; and the discovery of the coal-tar colours, to which the main credit is due to *Perkin*, has increased their resources almost indefinitely, for they are now able to match any ray of the solar spectrum. Before the time of alizarine and aniline (1858) the maker of coloured inks had recourse to the various vegetable and mineral products which have been used from time immemorial for dyeing fabrics. Thus for red he would employ Brazil wood and cochineal, the latter having a disadvantage in the circumstance that caustic ammonia in considerable quantity is necessary to dissolve it, so that it shall remain in solution and flow freely from the pen. But cochineal or carmine inks were expensive, and they, together with Brazil wood and tin-salt red inks, ceased to be manufactured to any great extent when the more brilliant coal-tar colours became available.

Older Formulæ for Coloured Writing Inks.—The following recipes, taken from various sources, are typical of the kind of coloured ink prepared from pigments other than aniline dye-stuffs:

Red Inks.—(i) Cochineal 1 oz.; ammonia, 1 oz.; and water, 1 quart; the infusion being decanted after three days, diluted with water to the required intensity of colour, and a little antiseptic added.

(ii) Brazil wood (powdered), 1 lb.; acetic acid (5 per cent. strength), 1 gallon, boiled until of sufficient colour, and the extract mixed with 8 oz. of gum, 8 oz. of alum, and a little antiseptic.

Green Inks.—(i) Cream of tartar, 1 part; verdigris, 2 parts, boiled with 8 parts of water.

(ii) Copper acetate, 1 oz. in 1 pint of water.

(iii) Potassium chromate, 10 parts; hydrochloric acid, 10 parts; alcohol, 10 parts; water, 30 parts. Neutralised with sodium carbonate after reduction to the chromic salt, mixed with 10 parts of gum, and decanted (*Winckler*).

(iv) Indigo ink mixed with a 1.25 per cent. solution of picric acid (*Stein*).

Blue Inks.—(i) Freshly precipitated Prussian blue triturated with a tenth of its weight of oxalic acid, and water gradually added.

(ii) Indigo carmine, 10 parts; gum, 5 parts; in 75 parts of water.

Purple Ink.—Infusion of logwood mixed with copper acetate, gum arabic and alum (*Normandy*).

Violet Ink.—Indigo blue ink mixed with cochineal ink.

Yellow Inks.—(i) A decoction of 25 parts of Persian berries (*Rhamnus amygdalinus*, &c.) in 100 parts of a 3 per cent. solution of alum mixed with 4 parts of gum.

(ii) A solution of gamboge in alcohol (10 : 10) mixed with 5 parts of gum and diluted to 30 parts with water.

(iii) A 10 per cent. solution of picric acid containing 2 per cent. of gum.

In a *Report* to the *Science and Art Department* in 1888, Dr. *Russell* and Sir *W. Abney* summarised the results of their experiments on the stability of various water-colour pigments exposed for two years to the action of light and dry air. In each case a wash of 8 tints was applied to paper of the same size and quality, and the slips enclosed in glass cylinders, so arranged that free circulation of air took place whilst dust was excluded.

In the following list, based on these results, the different pigments are arranged in the order of their instability, whilst those showing a distinct change in hue or depth of colour are marked with an asterisk: Carmine,* crimson lake,* purple madder,* scarlet lake,* Naples yellow,* olive green,* indigo,* brown madder,* gamboge,* vandyke brown,* Indian yellow,* cadmium yellow, sepia,* aureolin, rose madder, permanent blue, Antwerp blue, madder lake, vermilion, emerald green, burnt umber, yellow ochre, chrome yellow, raw sienna, Indian red, Venetian red, burnt sienna, chromium oxide, Prussian blue, cobalt, ultramarine ash.

When exposed to the action of moist air very few of the pigments remained unaffected, and none of those of organic origin, whilst the Prussian and Antwerp blues were completely destroyed.

Experiments were also made in which the washes of pigment were protected from the action of atmospheric oxygen and moisture. The vermilion turned black, but this change was attributed to a physical and not to chemical alteration.

In a later series of experiments, to quote Sir *W. Abney's* words:

"We took exactly similar tubes, dried the papers very carefully indeed, dried the tube, inserted the papers, put a Sprengel pump to work, and made a vacuum, and then when the vacuum was very complete, sealed off the top and exposed them." Under these stringent conditions only five colours were acted upon in the very least, and the amount of change was almost imperceptible. The five that were changed were vermilion, raw sienna, Prussian blue, purple madder, and sepia.

Coloured Aniline Inks.

Aniline Inks.—Any conceivable kind of red tint, from magenta to the most brilliant scarlet, can now be obtained from the makers of coal-tar colours, and the writers have to acknowledge their indebtedness to the *Badische Company, Ltd.*, for their courtesy in supplying full information as to the most suitable dye-stuffs, and sending specimen samples for testing. Some of these colours are more fitted for ink manufacture than others, those which are the more readily soluble in water being naturally the best. The red, known as eosine, which was discovered by Caro in 1874, was early recognised as a valuable material for the purpose, and appears to be more used than any other dye-stuff. In aqueous solution eosine is subject to the formation of a fungoid growth, so that a small quantity of an antiseptic must be added to the ink to keep it in good condition; otherwise its rich colour is liable to change.

As in the case of red inks, the manufacturer has a number of different tints of blue to choose from in the coal-tar colours. They are most tempting substances to employ, for the suitable ones form a true solution with water, and as a general rule nothing beyond water is required to convert them into serviceable inks. The first aniline colour which was tried for the purpose was Hofmann's violet, discovered in 1863, a dye-stuff of such high tinctorial value that an ink composed of one part of it in 200 parts of water not only gives a most vivid colour, but will afford by pressure three or four good copies.

Fugitiveness of Aniline Inks.—Instances of the instability of ink of this character, which is largely employed for typewriting, are given in a letter to the *Scientific American* (Ap. 18, 1903). The writer states that typewritten documents, after being stored for six months in a slightly damp place, were illegible, with the exception of the gall ink signatures.

In another case a letter-book was wetted with water used to extinguish a fire, and the signatures (in gall ink) were all that remained of 100 pages of correspondence.

It has also been shown by *Cross* and *Bevan* * that all the aniline colours when dyed on fabrics fade more or less on exposure to sunlight, whilst eosine and methylene blue are specially fugitive.

The following table of certain aniline dye-stuffs suitable for coloured writing inks is based on information supplied by the *Badische Company, Ltd.*

See also *Aniline Black Inks*, chap. v.; *Copying Inks*, chap. xii.; and *Ink Powders*, chap. xvi.

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* *Journ. Soc. Arts*, 1891, xxxix. 152.

Aniline Dye-stuffs suitable for Writing Inks.

Colour.	Trade name	Scientific
Red.	Eosine, erythrosine and phloxine.	Alkali salts of bromine and iodine compounds of fluorescein and of dichlorfluorescein.
	Ponceau scarlet.	Alkali salts of xylidin-azo- and cumidin-azo-naphtholdisulphonic acids.
	Cotton scarlet.	Sodium salt of amido-azo-benzol-azo-naphtholdisulphonic acid.
Green.	Neptune green S.G.	A triphenylmethane dye-stuff.
	Light green S.F. (yellowish).	Sodium salt of diethyl-dibenzyl-diamidotriphenyl carbinol trisulphonic acid.
	Light green S.F (bluish).	Sodium salt of the dimethyl compound.
	Diamond green G. & B.	Salts of tetra-ethyl- and tetra-methyl-di-para-amido-triphenyl carbidides.
Blue.	Indigo carmine.	Indigotin sodium disulphonate.
	Soluble blue T.	Salts of triphenylrosanilin and triphenylpararosanilin-trisulphonic acids.
Violet.	Acid violet 4B.L.	Sodium salt of tetramethyldibenzyl-pararosanilin-disulphonic acid.
Yellow.	Fast yellow.	Mixtures of the sodium salts of amidoazobenzoldisulphonic, monosulphonic, and amido-azotoluoldisulphonic acids.
	Tartrazine.	Sodium salt of diphenyl-parasulphonic acid or of azo-dioxytartaric acid.

The usual proportions that we have found to yield suitable solutions for writing inks are about 1 gramme in 50 to 80 c.c. of water, according to the tinctorial power of the particular dye-stuff. The inks thus made are very fluid, and in this respect particularly suitable for stylographic and other descriptions of fountain pens. If a suitable dye-stuff be used there will be no precipitation, and therefore no suspension of particles in the liquid. There is, therefore, no need to add gum to inks of this description; indeed, such an addition would tend to counteract one of their most valuable properties—their fluidity. It is necessary to mention this point, because we have found many published formulæ for aniline inks in which sugar or gum is erroneously included as a necessary constituent.

Patent Coloured Inks.—*Reade*, in his patent (No. 11,474, 1846), claimed the use of inks containing "soluble Prussian blue," prepared in a specified manner, and of a red ink prepared from cochineal. A lake of cochineal extract and alum dissolved in ammonia solution was also claimed by *Wood* in 1885 (Eng. Pat., No. 1676).

The use of aniline dyes was first claimed in this country by *Croc* in 1861 (Eng. Pat., No. 2972), and in the following year by *Lamand* (Eng. Pat., No. 675, 1862). Pigments from aniline waste were proposed as the source of writing inks by *de la Rue* (Eng. Pat., No. 2235, 1862), whilst aniline dye-stuffs were again patented by *Jefferies* in 1879 (Eng. Pat., No. 3391). For other patents in which coloured pigments are claimed see *Copying Inks*, *Sympathetic Inks* and *Ink Powders*.

CHAPTER VII.

EXAMINATION OF WRITING INKS.

CONTENTS.—Fluidity of ink—Penetration through paper—Stickiness of writing—Composition of commercial inks—Schluttig and Neumann's stripe test—Acidity, action on steel pens—Stability on keeping—**Examination of handwriting**—Old manuscripts—Palimpsests—**Forged handwriting**—Bleaching agents—Differentiation of writing done with different inks—Photographic methods—Mechanical erasure—Chemical removal of writing—Destruction of sizing—Alterations and additions to writing—Photographic distinction between different inks.

THE number of substances entering into the composition of ink is very large; but since the influence of many of these on the permanency of the writing is unknown, a full analysis of an ink would not afford much information, at any rate as compared with the results of practical tests.

One of the rules of the German *Versuchsamt* is that an ink for documentary purposes shall contain a certain minimum proportion of tannic or gallic acids derived from galls (*vide infra*). It has, however, been shown conclusively by *Schluttig and Neumann*, who submitted samples of different inks to the office for examination, that the chemical tests employed are quite incapable of identifying an ink prepared (*e.g.*, from chestnut bark), and they therefore contend that an ink prepared from tannic or gallic acid derived from any source should be permitted in inks of Class I.

The requirements of a good ink are: (1) It must yield permanent writing which becomes black within the course of a few days; (2) It must flow readily from the pen, and penetrate well into the fibres of the paper, without passing right through the paper; (3) It must not gelatinise or become mouldy in the ink-pots; (4) It should have a minimum corrosive action upon steel pens; (5) The writing must not be sticky (except in the case of some copying inks).

Fluidity of Ink.—*Schluttig and Neumann* recommend their stripe test (p. 121) as a means of determining the capacity of an ink to flow readily from the pen without spreading too freely on the paper. At the point where the glass pipette touches the paper in their test, an oval head to the stripe is formed, whilst the remainder of the stripe is nearly as wide. Of 81 inks examined by *Schluttig* and *Neumann*, the majority gave the same results as the typical ink, whilst the copying inks yielded somewhat narrower stripes. Inks flowing too readily, however, produced a much wider head, whilst the lower part of the stripe was contracted to a narrower band than the others.

We have found a simple viscosimeter, consisting of a 50c.c. pipette to give concordant results when used in the following manner. The pipette is standardised on distilled water at 15.5 C., the time required for the liquid to run down to a given mark on the lower stem being taken as *unity*. The ink is then brought to the same temperature, and the time taken for the same volume to run out determined in the same way. Thus, in a pipette from which the water ran out in 40 seconds, we found that different writing inks required from 42 to 55 seconds, whilst copying inks in some cases required 70 seconds.

Penetration through Paper.—This is best determined by a practical test on standard paper, under the same conditions as used with the typical standard ink. The ink should penetrate into the fibres, but should not come through the paper.

Stickiness of Writing.—Here, again, the best results are obtained by comparison with a typical ink, as recommended by *Schluttig* and *Neumann*.

Composition of Commercial Inks.—The following table gives the results of partial analyses of certain well-known commercial inks. It will be seen that the blue-black inks of the three different manufacturers are very similar in character.

Ink	Specific gravity at 15.5° C.	Water.	Total solid matter.	Ash.	Iron	Efflux viscosity (Water at 15.5° C. = 40 seconds).
		Per cent	Per cent.	Per cent.	Per cent	Seconds.
1 Blue-black I	—	96.21	3.79	0.704	0.32	—
2 „ I	1.0206	96.42	3.58	0.707	0.32	52
3 „ II	1.0214	96.44	3.56	0.90	0.27	40
4 Chrome ink	—	98.70	1.22	0.20	—	42
5 Japan ink	1.0113	92.74	7.26	2.18	0.81	55
6 Blue-black III	1.0141	97.44	2.56	0.58	0.23	43
7 Black ink (logwood) .	1.0115	97.86	2.14	1.04	0.14	43

A qualitative test that sometimes enables one to distinguish between inks of different makers is their behaviour on titration with a saturated solution of bromine water. Thus, the blue-black ink I. became first dirty grey, and then greyish-black; whilst No. II. first changed to violet and became turbid brown on the further addition of the reagent; and No. III. first became violet and then dirty green, the liquid remaining clear all the time. This last ink was also characterised by the ash being very difficult to burn white, and being then extremely insoluble in hydrochloric acid.

The presence of logwood in an ink is readily identified by the colour changing to bright red on the addition of hydrochloric acid (see p. 104). When indigo is also present the hydrochloric acid gives a purple coloration.

Indigo increases the stability of an ink towards bleaching agents such as bromine water. An ordinary iron gall ink is rapidly decolorised on the addition of strong hydrochloric acid, but if indigo be present the liquid remains blue, even after being boiled with the reagent.

Schluttig and Neumann's Stripe Test.—For comparison in their colorimetric method, *Schluttig* and *Neumann* make use of a standard ink containing the following constituents:—Gallotannic acid, 23.4 grms.; gallic acid, 7.7 grms.; gum, 10 grms.; hydrochloric acid, 2.5 grms.; and ferrous sulphate, 30 grms. in a litre of water. After standing for not less than four days, this ink is decanted and kept in a well-corked bottle.

In testing an unknown ink, 10 to 15 c.c. are compared with the standard ink, and should there be a difference in shade a small quantity of one or more suitable aniline dyestuffs is added to the standard, so as to make the colours match.

The apparatus required consists of a frame over which is tightly stretched a piece of best writing paper. This frame is fixed at an angle of 45°, and the unknown ink is allowed to run down this from a special pipette delivering exactly 0.6 c.c. A similar stain is made with the ink after dilution with an equal quantity of water, and also with the standard ink before and after dilution.

When the ink is dry the paper is set aside in a place exposed to light and air, and after eight days the stains are compared with the standard stains with regard to their colour, whilst their shape also gives an idea of the fluidity of the original ink. The paper is also to be cut in strips horizontally and one piece immersed in water, another in alcohol of 85 per cent. strength, and a third in alcohol 50 per cent. strength for several days. If the stripe of any particular ink becomes paler than that of the typical ink under these conditions, *Schluttig* and *Neumann* conclude that the former is either too poor in gallic or tannic acid, or contains too much acid.

The objects of repeating the test after dilution are that the added aniline colours have less disturbing influence in the diluted ink, that differences of intensity are more pronounced, and that differences in the breadth of the stripes given by copying inks are reduced to a minimum.

Schluttig and *Neumann* do not contend that all inks must have the composition of their typical preparation, but assert that while containing at least 0.6 per cent. of iron, they must give equally satisfactory results in the different tests.

In place of the somewhat complicated apparatus devised by *Schluttig* and *Neumann*, we have found that sheets of Bristol board placed on a wooden stand fixed at an angle of 45° give satisfactory and concordant results in this test.

Acidity: Action on Steel Pens.—It is not an easy matter to determine the amount of free acid in an ink by titration on account of the colour of the ink itself masking the change of colour of the indicator. It is possible, however, to obtain approximately correct results by diluting the ink with a very large volume of water and titrating with standard alkali, using phenol-phthalein as indicator. Thus in the case of a well-known blue-black ink we found that the acidity of 10 c.c. of the ink corresponded to 3.1 c.c. of normal alkali.

Another practical test is to immerse a steel pen in the ink for a given period, and to determine the loss in weight. Thus in the case of the ink referred to above we found that a pen had lost 5.18 per cent. of its weight after being kept in 10 c.c. of the ink for a month, whilst the ink itself had become nearly solid.

It is thus evident that the contention of *Schluttig* and *Neumann* [1] that free acid does not act upon metals in the presence of tannin is not justified by the results of experiments.

Schluttig and *Neumann* consider that it is not possible to fix a maximum amount of acidity. They recommend their stripe test as the best means of determining whether too much acid is present, since ink darkens more slowly the greater the proportion of acid. Thus, if the stripes are as intense a black in as short a time as those given by their standard ink, they consider the amount of acid as not too great.

Stability on Keeping.—A good ink will frequently keep as long as a year without throwing down any insoluble deposit on the sides of a vessel provided air be excluded. At the same time, if a sample bottle contain some deposit, the ink is not necessarily of bad quality, since this may be due to changes of temperature. Should there be a pellicle, however, in a sample bottle the ink should be rejected as inferior.

Schluttig and *Neumann* have devised the following test for determining the stability of an ink in a comparatively short time: The bottle containing the ink is allowed to stand for three days at a temperature of 10° to 15° C., after which 50 c.c. are withdrawn from the centre by means of a pipette without shaking the contents. This is filtered and 25 c.c. of the filtrate placed in a cylindrical glass vessel about 185 mm. high and 72 mm. in diameter, the mouth of which is then covered with paper to exclude dust.

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[1] *loc. cit.*

Schluttig and *Neumann's* typical ink when thus tested remained unchanged for three weeks, after which a pellicle began to form on the surface. and small flecks to separate out. This ink was obviously purer than ordinary commercial inks, many of which, however. remained unchanged for fourteen days or longer, and in *Schluttig* and *Neumann's* opinion this period should be fixed as the minimum keeping time for an ink of the first class under these conditions.

EXAMINATION OF HANDWRITING.

Old Manuscripts.—We have already pointed out that. although in many ancient manuscripts the writing is as distinct as when first written, there are also numerous cases in which the characters have faded to such an extent as to be almost illegible.

Numerous methods have been suggested for restoring the intensity of the original writing, but many of these are open to the objection that they injure the surface of the material.

The oldest and best known of these methods was to sponge the writing with an infusion of galls, the tannin of which would once more combine with the iron left in the paper, thus forming a fresh ink. This method was described in the book of *Canneparius* in 1660.

A much more reliable method was that first proposed by *Blagden* in 1787, which was based on the formation of a blue compound by the action of a solution of potassium ferrocyanide and dilute hydrochloric acid on the residual iron in the paper. This affords an easy means of distinguishing between carbon inks and iron gall inks, and *Blagden* was thus able to show that the writing on certain vellum manuscripts of the ninth and fifteenth centuries consisted of iron ink.

Lehner's method of applying this process of restoration s to immerse the paper for a few seconds in one per cent. pure hydrochloric acid, and to allow it to dry spontaneously. The writing is then dusted over with powdered potassium ferrocyanide, and covered with a glass plate on which is placed a weight. After being left for a few hours the paper is thoroughly dried, and the excess of ferrocyanide removed by means of a soft brush.

A more modern and less drastic method is to use a solution of ammonium hydrosulphide, which is applied for a few seconds until the writing becomes darker, and is then sponged off as rapidly as possible after the desired effect is obtained.

In this method the basic ferric salt into which the ink n the paper had decomposed is converted into the black ferrous sulphide. Writing thus restored may speedily be reoxidised so as to nearly disappear again, and the method can only be regarded as a temporary expedient. *Lehner*[*] has devised the following means of keeping writing thus restored for a longer period: The damped paper is supported on a frame of threads fixed half way up in a shallow box (four inches deep), whilst ammonium sulphide is placed in a small dish beneath. The box is closed by a glass cover, and after a short time the vapours of ammonium sulphide act on the writing, which becomes first brown and then black, and retains its intensity so long as the manuscript is left in the box.

Palimpsosts.—The name *palimpsest* is derived from the Greek words *παλιν* = again, and *πσιστος* = rubbed. It is applied to old manuscripts, the parchment of which had been previously used for a similar purpose. This practice was doubtless due to the cost of new material. The first writing on the skins was obliterated by means of pumice or some other abrading substance, but the mechanical action was insufficient to remove characters, possibly written three or four centuries earlier. In cases where the iron constituent of the ink had sunk deeply into the vellum, it would be almost impossible completely to eliminate it, and the use of the reagents described above would reveal the original characters.'

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[*] *Die Tinten Fabrikation*, p 144.

Morides' Process.—This consists of softening the skin by leaving it in distilled water, then treating it with a one per cent. solution of oxalic acid to bring the residual iron in the paper into a soluble state, again rinsing it in water and immersing it in a one per cent. solution of gallic acid, which will again form ink with the iron. Finally, the parchment is washed in water and pressed between blotting paper. Care must be taken to avoid an excess of oxalic acid, which might completely destroy the writing, and the method has the further drawback that the parchment is sometimes blackened all over by the gallic acid.

Lenher advocates exposing the parchment to steam and then to acetic acid vapours before applying the gallic acid.

It may also be noted here that photography affords a ready and most efficient means of deciphering such partially obliterated writing, the pale yellow colour of the iron oxide from the old ink appearing black in a photographic copy.

FORGED HANDWRITING.

The police reports abundantly prove that the crime of forgery frequently engages the attention of our magistrates. This is not surprising when we remember that the means are in the hands of every one, and that bankers' cheques are a common medium of exchange. The usual evidence called by the prosecution is that of the handwriting expert, who bases his opinion on the form and peculiarities of the caligraphy. We are inclined to think that much more stress might in many cases be laid upon the chemical aspect of the question. What we mean is that in a case where additional letters or figures have been added to, say, a banker's draft, it would be comparatively easy to ascertain whether the interpolated characters had or had not been written with the same ink as that used for the body of the document. When there is any objection to bringing chemical reagents in contact with the original paper, the camera can be employed in the way first brought into prominence by Dr Paul Jeserich, which we describe at length in a subsequent page.

Bleaching Agents.—It is possible to remove completely all traces of an ink stain (not containing carbon) by the use of suitable bleaching reagents, among which may be mentioned solutions of chlorine, bromine, acidified bleaching powder, &c.

Traill, in the course of his research into the permanency of inks, tested the effect of various reagents on the writing done with ordinary iron gall ink, and classified them into the following groups:—

I. *Those completely effacing the writing:*

Solutions of chlorine; chloride of lime with weak acid; antimony chloride; dilute *aqua regia*; and oxalic acid

II. *Those effacing the writing to a large extent:*

Dilute nitric, sulphuric, and hydrochloric acids.

III. *Those rendering the writing faint:*

Solutions of potassium and sodium hydroxides and ammonia.

To the first group we may add the following substances: Bromine, sulphur dioxide, sodium nitrite with hydrochloric acid, and citric acid; whilst hydrogen peroxide solution and potassium bisulphate speedily render the writing very faint.

As has been already mentioned, the addition of indigo to iron gall ink renders it much more resistant to the action of these reagents.

Differentiation of Writing done with Different Inks.—If writing from various sources be subjected to a systematic series of tests differences in that done with different inks, or even at different periods, will generally be observed. For instance, in the case of the reagents used by *Traill* (*supra*), fifty envelopes were tested, and the writing on no two of them gave identical results.

Robertson and Hoffmann[*] employed the following reagents for distinguishing between writing done with different kinds of ink. In each case a feather was dipped in the reagent and a note taken of any change occurring at the junction of the ink and paper.

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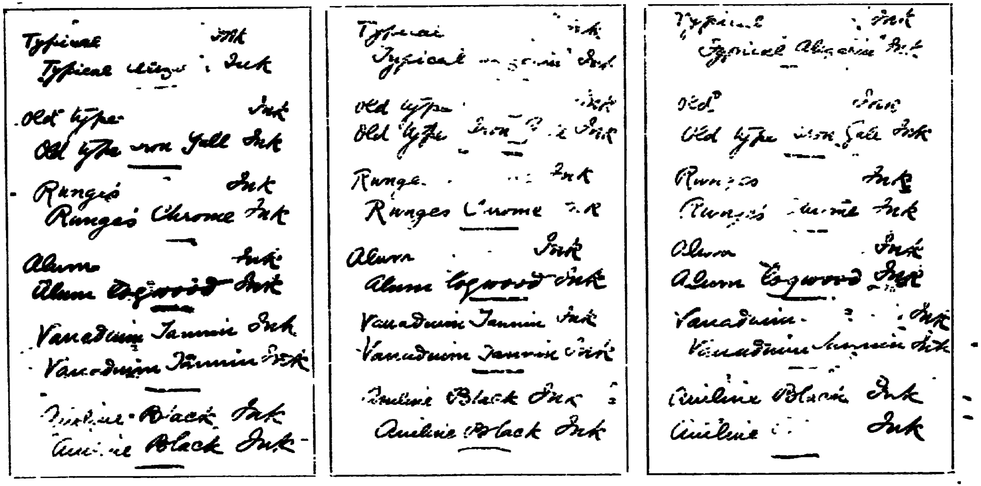
[*] Elsner, *Die Praxis der Chemiker*, p 598

Reagent.	Iron gall ink.	Logwood ink.		Nigrosine ink.	Vanadium ink.	Resorcin ink.
		Potassium chromate.	Copper sulphate.			
Oxalic acid, 3 %.	Bleached.	Violet.	Orange yellow.	Unchanged	Smudged and bleached.	Bright red.
Citric acid, 10 %.	Do.	Do.	Do.	Dark blue. smudged.	Do.	Bleached.
Hydrochloric acid. 10 %.	Faint yellow stain.	Purple red.	Blood red.	Hardly altered.	Slightly bleached, smudged.	Bright rose.
Sulphuric acid. 20 %.	Bleached.	Red.	Purple red.	Unaltered.	Slightly bleached.	" " red.
Nitric acid. 20 %.	Do.	Do.	Do.	Slightly smudged.	Do.	" " rose.
Stannous chloride, 1 : HCl, 1 : water, 10.	Do.	Do.	Red.	Unaltered.	Do.	Bleached.
Sulphur dioxide, saturated solution.	Do.	Violet grey.	Do.	Do.	Slightly bleached. smudged.	Do.
Gold chloride. 4 %.	Slightly bleached.	Red brown.	Brown.	Do.	Do.	Brown, smudged.
Sodium thiosulphate, ammonia and water (1 + 1 + 10).	Dark red.	Unaltered.	Dark blue.	Dark violet. smudged.	Very smudged.	Brown.
Potassium ferrocyanide + HCl + water (1 + 1 + 10).	Blue.	Red.	Purple red.	Unaltered.	Unaltered.	Rose.
Sodium hydroxide, 4 %.	Dark red.	Brown.	Dark red. smudged.	Dark violet. smudged.	Dirty brown. smudged.	Unaltered.
Chloride of lime. 2 %.	Bleached.	Bleached.	Yellow stain left.	Brown.	Unaltered.	Brown.

PLATE II


Typical Ink
Typical Ink
Old type Ink
Old type iron Gall Ink
Runge's Ink
Runge's Chrome Ink
Alum Ink
Alum Logwood Ink
Vanadium Tannin Ink
Vanadium Tannin Ink
Black Ink
Black Ink
Typical
Typical Ink
Old type
Old type Ink
Runge Ink
Runges
Alum Ink
Alum Logwood Ink
Vanadium Tannin Ink
Vanadium Tannin Ink
Black Ink
Aniline Black Ink
Typical Ink
Typical Alizarine Ink
Old type Ink
Runges Ink
Alum Ink
Alum Logwood Ink
Vanadium Ink
Aniline Black Ink
Aniline Ink

HYDROCHLORIC ACID OXALIC ACID BROMINE WATER

FIG. 29 ACTION OF BLEACHING AGENTS ON WRITING

In Fig. 29 we show the results of testing the writing done with different commercial inks with certain bleaching reagents.

Obviously these tests can only be looked upon as typical examples, for numerous other substances are added to modern inks, and each of these may play a part in modifying the reaction given by any particular reagent.

For the detection of forgeries in documents *Chevallier* recommended the following systematic series of tests: (1) Examination of the surface of the paper with a magnifying glass; (2) treatment with distilled water; (3) with alcohol; (4) with blue and red litmus; and (5) with various chemical reagents.

i. The colour of the ink is noted and any irregularities in the edges of the characters. If there has been any mechanical treatment the paper may appear thinner in some places than in others.

ii. Water may be absorbed more rapidly by one part than another.

iii. The object of the alcohol test is to detect removal of the size in the treatment which removed the writing. The writing on the rubbed part spreads out more and penetrates into the paper. Skilful forgers have employed rosin and glue to restore the surface of the paper. To detect this the paper is first treated with hot water and then with alcohol.

iv. The moistened document is placed between sheets of blue or red litmus on which is placed a weight, and a note taken of any change in colour and whether it is uniform.

v. The writing is moistened and treated with various intensifying reagents such as gallic acid, potassium ferrocyanide, alkali sulphide, or hydrogen sulphide, the treatment being repeated after twenty-four hours. Sometimes prior writing appears after the lapse of ten to thirty days.

Chevallier and *Lassaigne*[†] advocate the use of iodine vapour applied to the moistened paper, a blue spot appearing where the sizing has been erased, whilst the remainder of the surface becomes brown.

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[*] *Dingler's polyt. Journ.*, 1832. xliv. 131.

[†] Eisner, *loc. cit.*, p. 600.

The spots are then best treated with sulphur dioxide solution, then with a 3 per cent. solution of hydrogen peroxide, and lastly with ammonia. After removal of the excess of the last reagent tannin may be used to render any characters darker and more visible.

Potassium fluoride does not act upon indigo or aniline blue; but if characters made with Prussian blue be moistened with the solution and steam passed over them, white flecks appear.

Photographic Methods.—During the last twelve years considerable attention has been directed, especially on the Continent, to the application of the camera to the detection of alterations in manuscripts and printed matter. The chief advantages of photographic methods over chemical tests, if equally efficient, are that the document under examination is not affected in any way, and that details can be magnified to any required extent for closer examination. The latter consideration is of special importance in cases where a document forms the subject of inquiry before a court of law, and where it is necessary to demonstrate its characteristics to a judge and jury.

Mechanical Erasure.—We have previously noted that any obliteration of writing by mechanical means can almost invariably be detected by the eye, owing to the greater transparency of that portion of the paper. Such thinning of the paper would be detected still more surely by photographing it by transmitted light, the local injury appearing on the negative as a blot of greater density. If photographed in direct light the abrasion would probably not be apparent. If, on the other hand, the light were allowed to fall obliquely upon it, the roughened fibres would stand out distinctly unless some special means had been adopted for concealing the injury (*vide supra*).

Chemical Removal of Writing.—The slight yellow stain which is usually the effect of removing writing by the application of chemical reagents, though hardly noticeable to the naked eye, will be accentuated in the photographic negative.

Destruction of Sizing.—When writing has been removed by mechanical or chemical means, the size or other dressing on the paper may be simultaneously removed. This again would often be invisible to the eye, but would be readily revealed by the camera, for any ink marks on the rough places would spread to a certain extent over the now unshielded fibres of the paper. An enlargement of a few diameters only would render manifest the rough edges of the lines.

Alterations and Additions to Writing.—It is not difficult for a skilful forger to alter letters or figures so as to deceive the casual observer. Thus a 0 might be turned into a 6 or 9, or the word "eight" changed to "eighty." These alterations would be detected by a photographic enlargement.

Photographic Distinction between Different Inks.—*Jeserich*[*] was the first to assert that inks apparently black were really brown, blue, or red in tint, when dry upon the paper; and that such differences were clearly shown in an ordinary photographic negative, and still more so in one taken by the isochromatic method. This statement has been repeated by *Minorici*,[†] and quoted in different journals.

We have made experiments as to this point, writing a series of words with different commercial inks. Differences of intensity were distinctly visible to the eye, and the photograph taken on an ordinary plate by daylight revealed no more.

We have also photographed the same writing with a Cadett spectrum plate and "Absolutus" screen, without attaining any different effect. It is evident that this method, even if it yield good results in particular cases, is not generally applicable.

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[*] *Journ. Roy. Phot. Soc.*

[†] *Bull. della Soc. Fotograf. Italiana*, 1900, xii. 349.

SECTION III.

INKS FOR MISCELLANEOUS PURPOSES.

CHAPTER XII.

COPYING INKS.

CONTENTS.—Various copying inks—Patent copying inks—Copying papers—Copying ink pencils—Manifold copying apparatus.

MOST writing inks are capable of yielding one or more copies when pressed with a suitable moist paper soon after writing. Thus an ordinary iron gall ink of the old type will give a faint copy before it has become completely oxidised, but when once the pigment has become completely insoluble copies can no longer be taken.

As the process of copying tends to make the original writing too faint, it is necessary to have an additional quantity of pigment in the ink, together with a certain proportion of gum or other adhesive material to attach this excess of colouring-matter to the surface of the paper, and to protect it from too rapid oxidation.

In the case of "alizarine" inks the iron tannate becomes insoluble as the writing dries, but the indigo remains soluble in water, so that a faint blue copy can be taken at any subsequent period by pressing the writing with a damp sheet of paper.

Logwood inks yield reddish-grey copies, which gradually oxidise and become black. When the writing is completely dry only faint copies can be taken.

Dextrin is sometimes employed in place of gum to form a sort of varnish over the writing to prevent early oxidation. Sugar, too, is frequently added for the same purpose, but has the drawback of leaving the writing more or less sticky.

Viedt[*] considers that many copying inks contain too large a proportion of adhesive substance, and is of opinion that from 30 to 50 grms. of gum arabic per litre is quite sufficient for a good ink.

A small amount of glycerin is a common constituent of copying ink, its object being to prevent the gum from altogether drying. If, however, it be added in too large an excess the ink will smudge, as is the case with a certain commercial copying ink that contains as much as a third of glycerin.

Even in *Bottger's* copying ink (*infra*) the proportion of glycerin (120 grms. per litre) is too high, and in *Viedt's* opinion only a sixth of this amount is required to make an excellent copying ink on those lines.

Speaking generally, iron gall and logwood inks should contain from 30 to 40 per cent. less water than inks of the same formula intended for use as writing inks only.

Various Copying Inks.—Of the numerous published formulæ for copying inks the following are selected as typical, whilst others can easily be calculated by modifying the composition of writing inks given (pp. 93 99), in accordance with the general considerations given above:—

Stark's Patent Copying Ink.[†]—Logwood extract, 250 grms; iron sulphate, 17 grms.; copper sulphate, 17 grms.: alum, 100 grms.; and sugar, 50 grms., in a litre of boiling water. The solution is subsequently mixed with 16 grms. of potassium chromate, 100 grms. of glycerin, and 200 grms. of sulphindigotic acid.

Bottger's Alum Logwood Copying Ink.[‡]—One part of alum, 2 of copper sulphate, and 4 cf logwood extract are boiled with 48 parts of water, and the solution filtered.

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[*] *Dingler's polyt. Journ.*, 1875, ccxvii. 148.

[†] *Ibid.* 76.

[‡] *Ibid.*, 1859, cli. 431.

Copies made with this ink are faint at first, but soon become dark.

A later modification of this ink was made by *Böttger*[*] in the following manner:—Logwood extract 30 grms. and crystalline sodium carbonate, 8 grms. are boiled with 250 c.c. of water, and the solution mixed with 30 grms. of glycerin (sp. gr. 1.25), 1 grm. of potassium chromate, 8 grms. of powdered gum arabic, and (preferably) about 1 grm. of copper sulphate to strengthen the colour.

Débiton's Patent French Copying Ink.[†]—Galls, 10 grms.; ferrous sulphate, 100 grms.; and logwood, 300 grms.; are boiled with 1½ litres of water down to 1 litre. The solution is then mixed with 250 grms. of molasses, 15 grms. of gum, and 50 grms. of alcohol containing 5 grms. of an essential oil as preservative.

Dieterich's Violet Logwood Ink.[‡]—Logwood extract solution (20 per cent.), 600; sulphuric acid, 0·5; mixed with a solution of aluminium sulphate, 40; oxalic acid, 40; potassium carbonate, 40; potassium bichromate, 4; and phenol, 1; in 250 parts of water. This ink yields excellent copies.

Dieterich's Gall Copying Inks.—*Dieterich* [§] has prepared copying inks from oxidised gall extract and oxidised tannin solution prepared as described on p. 96.

Black Oxidised Gall Ink.—900 parts of the oxidised gall extract with 4 of sulphuric acid (sp. gr. 1.835) and 60 of ferrous sulphate, decanted after three weeks and diluted to a litre.

Black Oxidised Tannin Ink.—600 parts of oxidised tannin solution mixed with a solution of 60 parts of ferrous sulphate in 350 parts of water, filtered after three weeks and diluted to a litre.

For coloured copying inks, these inks are mixed with various aniline dyes, such as phenol blue 2·5 parts per litre; 6 of Ponceau red; 6 of aniline green; 1·5 of phenol blue and 2·5 of aniline green (for blue-green); 1·5 of phenol blue and 2.0 of Ponceau red (for violet), &c.

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[*] *Dingler's polyt. Journ.*, 1869, cxci., 75.
[†] *Wagner's Jahresber.*, 1873, xix. 872.
[‡] *Pharm. Manual*, 1897, p. 683.
[§] *Ibid.* p. 683.

Aniline Copying Inks.—Many of the commercial copying inks are prepared from aniline colours, which, being soluble in water and not undergoing oxidation, enable copies to be taken at any subsequent period.

Dieterich[*] gives the following formulæ for such aniline copying inks:—

Violet.—20 of methyl violet, 3 B, in 940 of warm water, with 10 of sugar, and 2 of oxalic acid.

Blue.—10 of resorcin blue in 950 of water, with 10 of sugar and 2 of oxalic acid.

Red.—Eosin, 25; sugar, 30, in 100 of cold water; subsequently filtered.

The following dye-stuffs manufactured by the *Badische Company* are suitable for copying inks:—

Violet Inks.—(*a*) *Crystal Violet*, the hydrochloride of hexamethylpararosaniline.

(*b*) *Methyl Violet* O and III. extra N, which are of similar chemical composition.

Green Inks.—*Diamond Green*, B and G (*cf.* p. 117).

Red Inks.—*Diamond Magenta* and *Magenta Powder*, which are mixtures of the hydrochloride and acetate of pararosaniline, and the corresponding salts of rosaniline respectively.

Safranine T. *extra*, being phenyl- and tolyl-tolusafranin chlorides.

Black Inks.—A combination of the above violets, greens, and reds with chrysoidine (diamidoazobenzol hydrochloride) yields a black copying ink.

Patent Copying Inks.—Numerous British patents have been taken out for the preparation of copying inks and papers, of which the following are the more important. The modern method of copying by means of pressure and a special ink is due to *James Watt*, the engineer (Eng. Pat., No. 1244; 1780), whose copying press was of the same form as in use to-day. The addition of glycerin was first claimed by *Henry* (Eng. Pat., No. 1132, 1858), whilst *Alberts* (Eng. Pat., No. 1213; 1862) added molasses and an extract of *allermoselt* seeds, in addition to glycerin. The use of glycerin was also claimed by *Winstone* (Eng. Pat., 1996; 1858), by *Cooke* (Eng. Pat., No. 47; 1869), and by *Coen* (Eng. Pat., No. 3247; 1891). In *Conrad and Lilley's* patent (No. 2011, 189[illegible]), indigo carmine, aniline black, glycerin and magnesium chloride are added to an ordinary iron gall ink; whilst the addition of a deliquescent salt, such as ammonium nitrate, with the glycerin is protected by *Conrad* (Eng. Pat., No. 10,401, 1890).

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[*] *Pharm. Manual*, 1897, p. 687.

Aniline dye-stuffs enter into the composition of several of the patented inks, that of *Kraysser and Hasak* (Eng. Pat., No. 4606; 1878), consisting solely of an aqueous or alcoholic solution of an aniline colour.

Copying inks in the form of a powder were patented by *Byford* (Eng. Pat., No. 974; 1876) and by *Jacobsohn* (Eng. Pat., No. 1580; 1878), the latter being prepared by evaporating to dryness a solution of aniline dye with sugar, gum, &c.

Copying Papers.—Of special copying papers that of *Pyford* (Eng. Pat., No. 10,905; 1890) was prepared by treating paper with a saturated solution of gallic acid, and was used with an iron ink. In *Bakes'* patent (No. 17,373; 1890), the paper consists of tissue paper saturated with a solution of loaf sugar and silver nitrate in a mixture of water and glycerin, whilst the ink is an iron gall logwood ink containing glycerin and vegetable black. Both of the above inks are stated not to require a copying press.

Another special copying paper is that protected by *Brown* (Eng. Pat., No. 3807; 1900), which is coated on one side with hardened gelatin, and on the other with a deliquescent salt such as calcium chloride and a solution of a substance not affected by ordinary ink. This paper does not require damping.

Copying Ink Pencils.—These consist of a base, such as powdered graphite and kaolin clay mixed with a very concentrated solution of methyl violet or other aniline dyestuff into a paste, which is pressed into sticks and dried. In *Viedt's*[*] opinion the use of gum arabic as a binding material is less suitable. Provisional protection was claimed by *Petit* (Eng. Pat., No. 4090, 1874) for a copying ink pencil prepared in this way.

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[*] *Dingler's polyt. Journ.* 1875, ccxvi. 90.

Manifold Copying Apparatus.—The well-known simple apparatus known as a *graph* is composed of a stiff gelatin bed, which receives the impression of the writing and enables several copies to be taken. The ink usually consists of an aqueous solution of methyl violet or other soluble aniline dye This type of copying apparatus was patented by *Rosefeld* in 1879 (Eng. Pat., No. 2256), the block consisting of gelatin, glycerin, molasses or sugar, acetic acid, and iron oxide, with sodium bisulphite to prevent decomposition of the gelatin. Special aniline and metallic inks for manifold copying apparatus were also patented by *Hardt* (Eng. Pat., No. 4187; 1879).

Another copying apparatus of the same type, protected by *Schmitt* (Eng. Pat., No. 948; 1881), contained glycerin and chrome alum in the jelly, whilst the ink contained a colour, such as indigo and a uranium salt, and had a chemical action on the bed. The impression produced on the bed was capable of receiving printing ink. The drawback of gelatin copying apparatus is that the jelly soon becomes saturated with the aniline ink and is no longer capable of yielding clean copies. This is obviated in the apparatus protected by *Smith* (Eng. Pat., No. 7149; 1888), which consists of a slab composed of a mixture of china clay, starch, glycerin, and water, from which the impression can be completely removed by means of a sponge after use. The ink is a solution of an aniline colour in a mixture of water, alcohol, and hydrochloric acid.

CHAPTER XIII.

MARKING INKS.

CONTENTS.—The ink plant of New Granada—The Indian marking nut—The Cashew nut—Rhus toxicodendron—Rhus venenata—Rhus radicans—Other vegetable juices—**Chemical marking inks**—Silver inks—Gold marking inks—Platinum marking inks—Marking inks containing other metals—Aniline marking inks—Indigotin marking inks—Alizarine marking ink—Examination of marking ink—Marking ink pencils.

NATURAL VEGETABLE INKS.

NUMEROUS plants contain a juice, which is oxidised on exposure to the air, yielding black or brown pigments, often of great durability; and such natural inks have been employed in various parts of the world, either for writing or for marking linen.

Jametel,[*] quoting from ancient Chinese documents, states that prior to about 2697 B.C. the Chinese used a kind of vegetable varnish for ink, and not the product which is now known as Chinese or Indian ink. It is probable that this ink was the juice of a species of *Rhus* (*vide infra*).

The Ink Plant of New Granada—According to *Johnson*[†] the juice of *Coriaria thymifolia*, known locally as *chanci*, or the "ink plant," is at first red, but rapidly changes in colour, becoming deep black in a few hours.

The juice can be used as ink without any treatment, and gives a very stable writing, which is not affected by sea-water. *Johnson* states that all the older documents in Spanish South America were written with this ink.

It is also a native of New Zealand, where too it goes by the name of the "ink plant."

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[*] *Loc. cit.*, Introd. p. x.

[†] *Universal Cyclopedia*, New York, 1894, art. *Ink*.

[‡] Smith, *Dict. of Econom. Plants*, p. 132.

The Indian Marking Nut.—The fruit of the Indian tree *Anacardium orientale*, which is now termed *Semecarpus anacardium* (Fig. 42), has long been known as the "marking nut," from the fact that its juice makes a very dark and durable stain on linen or paper.

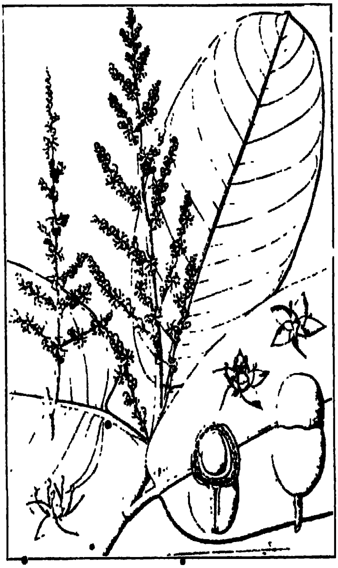

Fig. 42.—Indian marking nut (*Semecarpus anacardium*).

The tree is found throughout the hotter parts of India, though not in Ceylon, and is also met with in the West Indies and in Northern Australia. The ripe fruit is yellow in colour, and is eaten after roasting by the natives. As met with in commerce it is a black oval or heart-shaped substance, about 2 cm. in length, and the same in breadth, and ½ cm. thick. The white kernel is covered by a reddish pellicle.

The natives prepare the ink from the unripe fruit, and use it when mixed with quick lime for marking cotton and linen, on which it produces a very permanent mark.[*] The dried juice is also extensively employed in the manufacture of a black varnish.

Lewis[†] found that the juice required warming to make it flow freely. The writing done with it was first reddish brown, but rapidly became deep black and was very indelible.

The brown oil from the mesocarp dissolves in potassium hydroxide solution, giving a green solution, whilst the alcoholic solution becomes black on the addition of basic lead acetate.

The juice has a very irritant action upon the skin, producing symptoms similar to eczema, and the same effect is said to be produced by the fumes given off on roasting the nut.

We have made a number of experiments with the dried nuts. The black viscous juice surrounding the kernel of these had a characteristic aromatic odour and produced a light brown stain, which gradually darkened on exposure to the air.

A decoction of the broken nuts in boiling water rendered alkaline with ammonia yielded a dark fluid, and the characters made with this on paper or linen were dark brown, and very resistant to the action of reagents. They were not removed by bromine, oxalic acid, or hydrochloric acid, whilst alkalies rendered them darker. They were soluble, however, in ether.

Kindt's[‡] method of preparing the ink was to extract the nut with a mixture of absolute alcohol and sulphuric ether to evaporate the extract to the required consistency. The writing done with this fluid on the linen was moistened with lime water or an alkaline solution to turn it black. *Kindt* found that it was capable of resisting boiling with hydrochloric acid and potassium chlorate, though rendered faint by the treatment.

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[*] *σημεῖον* = a mark, and *καρπός* = fruit.

[†] *Philosophico-Technicum*, 1765, p. 329

[‡] *Dingler's polyt. Journ.*, 1859, cliv. 158.

The Cashew Nut.—This is the fruit of another member of the *Anacardiaceæ*, *A. occidentale* a tree somewhat

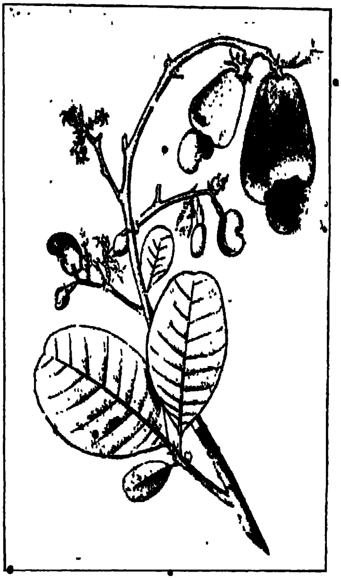

Fig. 43.—Cashew nut (*Anacardium occidentale*).

resembling the walnut in size and appearance (Fig. 43). It is found in India, the West Indies, and tropical parts of South America.

The kidney-shaped fruit is about an inch in length, and projects from a fleshy pear-shaped fruit-stalk. The milky juice in the stem of the tree becomes hard and black on exposure to the air, and is used locally as a varnish.

Lewis[*] in 1763 found that the dark viscous juice within the nut when applied to cotton or linen gave a brown stain, which was very permanent, but did not become black upon exposure to the air.

The brown oil in the fruit is soluble in potassium hydroxide solution. On treating an alcoholic solution with basic lead acetate a red preciptate is obtained.

In 1847 *Stadeler* separated a vesicating principle, which he termed *Cardol* ($C_{21}H_{30}O_2$), and a reddish yellow oil, which he termed *Anacardic acid*.

Rhus toxicodondron.—This is a poisonous plant, originally indigenous to N. America, where it was known as the "poison tree" by the natives of Carolina,[†] and to Japan, where the juice has long been used as a varnish.[†]

The milky juice rapidly darkens on exposure to the air, and has frequently been recommended as an indelible ink, especially for marking linen. Thus the *Abbé Mazeas*[‡] stated that he had made experiments on this point, and found that the writing still remained black after five years, during which period the linen was repeatedly washed.

The plant, which is also known as the *poison ivy* and *poison oak*, grows to a height of several feet, and produces small green flowers (Fig. 44). The leaves are employed commercially in the manufacture of a black stain, and are collected for this purpose from May to July, whilst the plant is in bloom. The juice of the leaves will raise a blister on the skin within forty-eight hours, and even the vapours given off by the living plant, especially by night, produce vesicular eruptions on the skins of certain people peculiarly sensitive to its effects. *Porcher* found that the acrimonious vapours emitted during the night contained hydrocarbons, and would ignite when brought into contact with a flame.

Khittel, who examined the constituents of the plant in 1858, found that it contained an "iron-greening" tannin.

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[*] *loc. cit.*

[†] Miller, *Trans. Roy. Soc.*, 1755, xlix. 161.

[‡] *loc. cit.*, xlix. 157.

In 1865 *Maisch* and *Stillé** isolated a volatile substance which reduced silver nitrate solution and gave a white precipitate with lead acetate, and a white precipitate, turning black on heating, with mercurous salts. To this substance they gave the name of *toxicodendric acid.*

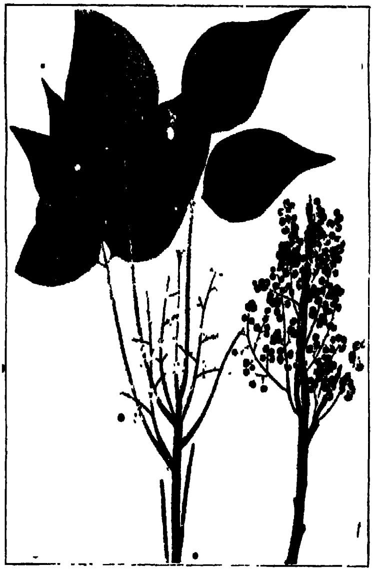

Fig. 44.—*Rhus toxicodendron.*

Their results were confirmed in 1883 by *Pettigrew,* who also found that the acid gave a red colour with ferric salts.

The black stain produced by the juice of *R. toxicodendron*

National Dispensatory, p. 1382.

cannot be removed by the treatment with alcohol or soap and water, but dissolves in ether.

Rhus Venenata.—This is a shrub which grows on marshy ground in North America, where it is popularly known as the *poison sumach*. It is usually from 10 to 15 feet high, but sometimes reaches a height of 30 feet. It has a dark grey bark, and produces greenish-white flowers and berries.

On making an incision in the bark a thick white, opaque, pungent fluid exudes, which on exposure to the air rapidly becomes black. When this liquid is boiled with water the volatile constituents are expelled, and the residue can be used as a black varnish, similar to that prepared from the *Rhus vernicia* of Japan.

The poisonous symptoms caused by the juice are similar to those produced by *Rhus toxicodendron*, but many persons are quite immune to its effects, whilst others are more affected by its emanations than by those of *R. toxicodendron*.

The workmen who use it as a finishing varnish for boots frequently suffer from its action.*

Rhus radicans is a variety of *R. toxicodendron*, and not a separate species. It produces round greenish-white berries, and its juice has similar properties.

Other Vegetable Juices.—*Lewis* in 1763 made numerous experiments to determine the permanency of the stains produced by the juices of different plants. He found that the milky juices of poppies, dandelion, hawkweed and sowthistle gave brown or brownish-red characters, but that these were readily removable on washing the linen.

The colourless juice from hop stalks, on the other hand, gave a very permanent pale reddish-brown stain.

Sloe juice.—The juice from sloes used by itself gave a pale brown stain, whilst with the juice used in conjunction with alkali a much darker stain was produced. The fresh juice, on baking, became red, and when applied to linen gave red stains, which became blue on contact with soap. These characters were very permanent, and had only become faint after long continued washing.

* Millspaugh. *American Medicinal Plants*, p. 37.

CHEMICAL MARKING INKS.

Silver Inks.—Of the different substances that have been employed as marking inks, the best known and most commonly used has been a solution of a silver salt, the reduction of which within the fibres of the material has left an insoluble black deposit of a more or less permanent nature.

The earliest inks of this type required the linen to be previously treated with what is known as a *pounce* and then dried, but these have been entirely superseded by inks which are reduced by passing a hot iron over the writing.

An ink of this earlier type was recommended by *Reimann** as late as the year 1870. It contained 1.6 parts of silver nitrate, 2 parts of gum arabic, ⅓ part of sap green in 16 parts of water; whilst the pounce consisted of 2 parts of crystalline sodium carbonate and 2 parts of gum in 8 parts of water.

A similar ink intended for use with steel pens was also described by *Reimann*. It was prepared by dissolving 2 parts of silver nitrate and 2½ parts of gum in 5 parts of ammonia solution and filtering the liquid, a little magenta red being added to impart a temporary colour. The *pounce* for this ink contained 3 parts of sodium carbonate with 2½ parts of gum in 9 parts of water.

Redwood's Marking Ink.—This was prepared by adding a solution of 31 parts of silver nitrate in water to a solution of 50 parts of sodium carbonate in water, collecting and washing the precipitated silver carbonate, triturating it with tartaric acid and adding sufficient ammonia solution to dissolve the silver tartrate. The ink was then completed by the addition of 15 parts of archil extract, 16 parts of white sugar, and 50 parts of gum arabic. With this ink no previous preparation of the fabric was necessary, a hot iron being passed over the writing to start the reduction.

Some time afterwards *Reade* (Eng. Pat., No. 11,474; 1846) claimed the use of a marking ink the basis of which was also silver tartrate. This was prepared by rubbing together in a mortar equal parts of tartaric acid and silver nitrate, then adding water, and finally neutralising the liquid with ammonia. In this process the somewhat tedious operation of washing the silver carbonate, as in *Redwood's* process, was dispensed with.

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* *Dingler's polyt. Journ.*, 1870, cxcv. 281.

Claim was also made for the addition to this ink of an ammoniacal solution of a gold salt, so as to render the writing proof against the action of solvents for silver salts.

Dieterich (1897) recommends a solution of 25 parts of silver nitrate and 15 of gum in 60 parts of ammonia solution, with the subsequent addition of 2 parts of lamp-black or indigo as a temporary colouring-matter.

The ink is used with a quill pen, and the writing is fixed by passing a hot iron over it. By increasing the amount of gum to 25 parts, a rubber stamp can be used with the ink.

Soehnée's Marking Ink[*] consisted of 8 parts of silver nitrate, 4 parts of sodium carbonate, and 3 parts of copper nitrate, in 100 parts of ammonia solution.

Bufton (Eng. Pat., No. 738; 1856, *Proc.*) claimed the addition of platinum chloride to a silver marking ink, with the object of rendering the characters more permanent.

Kindt's Marking Ink[†] consists of 11 parts of silver nitrate dissolved in 22 parts of ammonia solution and mixed with a solution of 22 parts of sodium carbonate in 12 parts of water. The ink is then thickened by the addition of 50 parts of gum and coloured with 2 parts of sap green. Marks made with this ink on linen gradually darken on exposure to light, but the process of reduction is accelerated by heat.

Silver Chloride Marking Ink.—The linen fabric is first prepared with a 20 per cent. solution of sodium chloride, to which has been added 50 per cent. of gum arabic. The ink is prepared by dissolving 1 part of silver nitrate and 2 parts of gum, in 10 parts of water, and adding a little indigo carmine as temporary colouring-matter. The silver nitrate in the ink reacts with the sodium chloride in the prepared linen, forming silver chloride, which is reduced on exposure to sunlight.

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[*] *Dingler's polyt. Journ.*, 1848, cviii. 157.

[†] *Ibid.*, 1859, cliii. 393.

*Kuhr's Marking Ink.**—Very black characters are produced by an ink consisting of 1 part of silver nitrate and 6 parts of gum arabic in 6 parts of water, on linen previously prepared with a solution of 1 part of sodium hyposulphite and 2 parts of gum in 16 parts of water.

Gold Marking Inks.—One of the best known gold inks is based on the formation of what is known as the *purple of Cassius*. The linen is prepared by treatment with a 1 per cent. solution of stannous chloride containing 10 per cent. of gum, whilst the ink consists of a 1 per cent. solution of the double chloride of gold and sodium, to which also has been added 10 per cent. of gum.

If the fabric be prepared with a 20 per cent. solution of oxalic acid containing 40 per cent. of gum, instead of with the tin solution, the gold writing has a metallic lustre after being ironed and washed.

Gold marking ink is more permanent than silver ink, and its addition to the latter was patented by Reade (*supra*).

Platinum Marking Inks.—These are prepared in two solutions like the gold ink. The fabric is first treated with a mordant containing 30 parts of oxalic acid and 30 parts of gum in 100 of water and dried. The ink, which consists of 1 part of platinum chloride and 2 parts of gum in 10 parts of water, produces red marks on the prepared linen, which should be well washed as soon as the writing is dark enough.

A purple platinum marking ink described by *Reimann* (*loc. cit.*) contains 1 part of platinum chloride in 16 parts of water. The linen is first prepared with a solution of 3 parts of sodium carbonate and 3 parts of gum in 12 parts of water and dried. After the letters have been written on this prepared surface and have dried, the place is moistened with a solution of 1 part of tin chloride in 4 parts of water, which changes the writing to reddish purple.

Marking Inks containing other Metals.—In addition to platinum and gold salts, which have been used either alone or in conjunction with silver salts as constituents of marking inks, and which are obviously too expensive for general use, numerous other metallic compounds have been employed for the same purpose. Thus in 1878 *Hickisson* (Eng. Pat., No. 5123) protected an ink containing a salt of vanadium with an oxidising agent composed of metals or salts preferably those of nickel and copper, to act as mordants.

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* *Dingler's polyt. Journ.*, 1867, clxxxv. 326

Sachs (Eng. Pat., No. 1838; 1880) has produced solutions which he claims to be good marking inks, by the action of polysulphides of heavy metals, such as those of iron, zinc, or copper, on organic substances, such as non-volatile fats or sawdust, in the presence of a suitable metallic hydroxide or sulphide, *e.g.*, sodium hydroxide or sodium sulphide.

Marking inks of various colours were protected by *Langbeck* (Eng. Pat., No. 5946; 1882). These consisted of pigments, such as gas-black, vermilion, ultramarine, cadmium yellow, and emerald green, mixed with a suitable proportion of albumin, and incorporated with a liquid base composed of salicylic acid, turpentine oil, spirits of wine, glycerin, and water in approximately specified proportions. In a subsequent patent (No. 751; 1883) taken out by *Hickisson* and *Langbeck*, the basis of the ink made from these pigments was a solution of india-rubber in carbon bisulphide, a little essential oil being added to prevent too rapid evaporation. The fabric was heated after marking. In yet another method, protected by the same patentees (No. 752; 1883), the mixture of pigments and albumin was added to a base consisting of 5 to 8 grains of arsenic pentoxide, 10 grains of turpentine oil, 6 drachms of glycerin, and 1 oz. of water.

Dimitry's Bichromate Marking Ink (Eng. Pat., No. 648; 1888) consists of a soluble colouring matter mixed with gelatin and potassium bichromate, this last constituent being reduced on exposing the writing to the action of sunlight.

Molybdic Marking Ink.—An ink was recommended by *Roder** in 1856 as adhering well to the linen, and resisting the action of both acids and alkalies. It was prepared by dissolving 5 parts of molybdic oxide in sufficient hydrochloric acid, and adding 6 parts of gum arabic and 2 parts of sweetwood extract (*Lakritze*) in 30 parts of water. When the writing was dry the linen was treated with a solution of tin chloride.

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* *Dingler's polyt. Journ.*, 1856, cxli. 150.

Copper Marking Inks.—The precipitate obtained on treating a solution of copper chloride with potassium hydroxide is dissolved in as little ammonia solution as possible, and a little dextrin or gum added as a thickening agent. The writing done with this ink becomes black when a hot iron is passed over it.

Seyffern (Eng. Pat., No. 1744; 1859) protected a process of making an ink for marking cloth, paper, &c., by immersing organic fibrous material, such as silk, in ammonia solution containing copper, and admitting air through a small opening from time to time. The solution of silk in this "copperised ammonia" was described by the inventor as a "lustrous black ink."

A Blue Indelible Ink recently described * consists of a mixture of a silver and a copper marking ink. (*a*) Silver nitrate 10 parts in 30 parts of ammonia solution. (*b*) Sodium carbonate 10 parts, gum arabic 15 parts, and copper sulphate 5 parts in 40 parts of water. The two parts (*a*) and (*b*) are mixed together.

Manganese Marking Ink.—*Reimann* (*loc. cit.*) recommends the following as a cheap brown marking ink. The linen is first prepared by treatment with a solution of 1 part of a ferrocyanide and ½ part of gum in 3 parts of water and dried. The writing is then done with a solution of 4 parts of manganous acetate in 12 parts of water, and the linen finally treated with a solution of 4 parts of potassium hydroxide in 10 parts of water.

This causes the separation of manganese hydroxide, which is gradually oxidised, forming a dark brown manganese oxide.

This process is manifestly too complicated for ordinary use, and the treatment of the linen with strong caustic alkali solution must have an injurious effect upon the fibres.

Aniline Marking Inks.—An ink in one solution is obtained by thoroughly mixing 2 parts of aniline black in

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* *Scient. Amer. Suppl.*, June 31, 1902.

40 parts of strong alcohol (95 per cent.) containing 2 parts of hydrochloric acid, and adding a solution of 3 parts of shellac in 150 parts of the strong alcohol. The writing done with this ink is not removed by water, but is not very resistant to the action of alkalies.

*Jacobsen's Aniline Ink.**—This ink depends on the formation of aniline black within the fibres.

It consists of two solutions, which are kept separate until just before use:

(*a*) *Copper Solution.*—Copper chloride, 8.52 grms.; sodium chlorate, 10.65 grms.; and ammonium chloride, 3.35 grms., in 60 c.c. of water.

(*b*) *Aniline Solution.*—Aniline hydrochloride, 20 grms., dissolved in 30 c.c. of water, and mixed with 20 grms. of a solution of gum arabic (1 : 2) and 1 grm. of glycerin.

For use, 1 part of (*a*) is mixed with 4 parts of (*b*). The writing on linen first appears green, and then gradually becomes black on exposure to the air. The change takes place at once on heating the fabric, but it is advisable to hold it over steam, since dry heat tends to render the marked places brittle. Finally the place should be washed in soapy water, which renders the writing blue-black. Marking properly done with this ink resists the action of acids and alkalies, and can be frequently washed without being rendered much fainter.

Indigotin Marking Inks.—The so-called indigo blue when pure is known in chemistry as *indigotin* ($C_{16}H_{10}N_2O_2$). When this is treated with a reducing agent it is converted into a colourless compound, *indigo white* ($C_{16}H_{12}N_2O_2$), which is readily soluble in solutions of alkalies, and has only to be exposed to the air to be gradually oxidised again into the insoluble blue compound.

An indigo marking ink based on this reaction is prepared by treating a mixture of 20 parts of indigo blue powder and 40 parts of ferrous sulphate with a solution of 40 parts of sodium hydroxide in 200 parts of water. The whole is then left for several days in a well-corked bottle, which is shaken from time to time until the reduction is complete, and all sign of blue has disappeared. The liquid is then decanted, and 20 parts of gum arabic added to 1 part

* *Dingler's polyt. Journ.*, 1867, clxxxiii. 78.

of a saturated solution of litmus to form the provisional colouring-matter. The writing done with this ink is soon oxidised by the atmospheric oxygen, and eventually becomes deep blue. The same oxidation gradually takes place in the ink, with the formation of a blue deposit in the bottle.

A marking ink patented by *Johnson* (Eng. Pat., No. 1771; 1880) is based on the synthetical formation of indigo blue within the fibres of the fabric. The material is treated with a solution containing ortho-nitro-phenyl-propiolic acid, a reducing agent such as glucose, and a fixed caustic or carbonated alkali. The writing is developed by the action of steam, which produces a blue colour, or by dry heat, which makes it black.

Alizarine Marking Ink.—A red marking ink, containing the pigment of madder (alizarine) as its basis, was patented by *Moller* in 1864 (Eng. Pat., No. 2511). The linen was first prepared by treatment with a solution of alum, and the marking done with an ink composed of an alcoholic extract of madder mixed with an alkali salt, gum, and vermilion.

Examination of Marking Inks.—The chief essentials of a good marking ink are: (1) It shall not injure the fibres of the fabric; (2) it shall not be too viscous to flow smoothly from the pen, and yet not so fluid as to "run" when applied to the linen; (3) it shall produce characters which rapidly darken when treated with a moderately hot iron or otherwise; (4) the characters shall not fade when repeatedly washed with soap and water, and shall resist the action of acids, alkalies, and bleaching-powder.

The composition of an ink is of subsidiary importance as compared with the results of practical tests. It is best to make characters both on linen and fine fabric, and to follow the manufacturer's directions for the subsequent treatment of the material.

Marking Ink Pencils.—The earliest pencils intended for marking linen contained a silver salt incorporated with a suitable basic material and a provisional colouring-matter. In *Dunn's* patent (Eng. Pat., No. 2316; 1858) plumbago is mentioned as a suitable substance to be mixed with the silver salts.

A similar pencil was patented by *Schroll* (Eng. Pat., No. 379; 1877). This was composed of a suitable clay earth mixed with silver nitrate or other soluble silver salt, and plumbago freed from impurities that would cause reduction in the silver salt.

In 1878 *Hickisson* (Eng. Pat., No. 5122) adapted his vanadium marking ink (*supra*) to the preparation of marking ink pencils, gum, gelatin, dextrin, clay, or other suitable substance being added, and the mass moulded into the required shape.

Marking pencils giving different coloured characters were prepared by *Hickisson* and *Langbeck* (Eng. Pat., No. 752, 1883) from the marking inks containing a suitable pigment and albumin in a liquid base of arsenic pentoxide, turpentine oil, glycerin, and water.

A silver pencil also patented by *Hickisson* (Eng. Pat., No. 9149; 1884) has a marking-point which may consist of silver nitrate and potassium nitrate, or in some cases ammonium carbonate, fused with gum, whilst the other end of the pencil contains a mordant composed of, *e.g.*, borax, wax, and pyrogallol, which is applied to the writing to fix it. In a subsequent patent (Eng. Pat., No. 15,961; 1884), claim is made for separate pencils containing only the mordant. Aniline dye-stuffs soluble in oil, claimed by *Hickisson* (*supra*) are also made the colouring material in marking pencils. For this purpose they are incorporated with suitable ingredients, such as gum tragacanth, kaolin, and borax, into a solid mass. The linen fabric is damped with a suitable oil, such as castor oil, and the writing finally heated.

In our experience with certain marking ink pencils of foreign origin containing aniline dye-stuffs, the writing is of a very fugitive character.

CHAPTER XIV.

SAFETY INKS AND PAPERS.

CONTENTS.—**Various safety inks**—Resinous inks—Traill's carbon gluten ink—Soluble glass ink—Other carbon inks—**Safety papers with special inks—Patent permanent inks—Patent safety papers.**

THE term "safety" has been frequently applied to inks which are supposed to resist the action of all chemical agents not sufficiently powerful to destroy the paper or parchment itself. The importance of such an ink in the case of historical records or legal documents, &c., is obvious, and numerous experiments have been made to discover the best fluid for the purpose.

It has already been noted in the introduction that iron gall inks may, under favourable conditions, almost equal carbon inks in defying the ravages of time, although many instances can be cited where inks of the same character have prematurely faded. It may be pointed out in connection with this imperfection that chlorine is used as a bleaching agent in paper manufacture, and although "antichlor" (sodium thiosulphate) is used to remove free chlorine, cases may occur in which a trace of the chlorine is left, and would then have an effect upon an iron ink.

Various Safety Inks.—Several of the earlier formulæ for producing permanent writing fluids have already been described in chap. i., in the section dealing with carbon inks, p. 34.

Inks recommended by French Commission.—In 1831 a Commission appointed by the Paris Académie des Sciences, and including such eminent chemists as Gay-Lussac and Chevreul, made a critical examination of all the inks that had been proposed up to that time for the prevention of the falsification of writing, and concluded that prior to 1826 none was satisfactory. They were either too thick, or attacked the paper, or yielded a deposit too readily. Of the different inks submitted, the Commission recommended the two following:

i. Indian ink (4 to 5 grms.) mixed with 1000 grms. of dilute hydrochloric acid (2.010 sp. gr.). This ink flowed well and had good penetrating power, whilst the acid did not injure the paper.

ii. A solution of manganese acetate (sp. gr. 1.074). With a ninth of its volume of acetic acid (100 parts neutralising 160 of sodium carbonate), thoroughly incorporated with Indian ink. The writing was then fixed and rendered indelible by holding it over ammonia vapour.

The advantage of this ink over the preceding one is that the paper will not contain free acid.

We have prepared carbon inks from these formulæ, and find that the writing resists the action of water, acids, and bleaching agents. In the case of the first ink, however, we find the quantity of Indian ink mentioned quite insufficient. We used the finest that we could obtain, and had to add at least six times as much in order to obtain characters of sufficient blackness. After the treatment with ammonia vapour the writing becomes much greyer.

MacCulloch[*] used a solution of potash and wood tar, whilst *Thomson*[†] mixed lamp-black with a solution of shellac and borax.

Resinous Inks.—This last ink is very much on the lines of that described by *Desmarest*,[‡] viz., shellac, 15; borax, 8; gum arabic, 8; lamp-black, 10; and water, 130 parts. The powdered shellac and borax are boiled with the water, and the solution mixed with the powdered gum and lamp-black, and eventually decanted from the heavier particles.

In 1837 *H. Stephens* and *E. Nash* patented (Eng. Pat., No. 7342) the addition of carbonaceous matter to saline or alkaline solutions of resinous substances to form compounds not attacked by ordinary chemical agents (*vide infra*).

[*] *Ann. de Chim. et Phys.*, 1831, xlviii.

[†] *Ibid.*

[‡] *Les Encres et Cirages*, 1895, p. 141.

An ink of this character is prepared by boiling 10 parts of ordinary rosin and 10 parts of sodium, potassium, or ammonium carbonate, either alone or, preferably, mixed in equal proportions, with 100 parts of water, and adding a mixture of 4 parts of powdered gum, and 2 parts of lamp-black.

Traill's Carbon Gluten Ink.[*]—This consisted of lamp-black and indigo incorporated with an acetic acid solution of the gluten of wheat flour. The gluten was prepared by kneading the flour in a current of water until the starch has been separated. After twenty-four to thirty-six hours in the water it was digested with acetic acid (sp. gr. 1.033 to 1.034) in the proportion of 20 to 3 of gluten. The grey liquid eventually obtained with the aid of gentle heat was then used as the medium for the pigment, which consisted of about 2 per cent. of purified lamp-black, and about ½ per cent. of indigo.

An ink attributed to *Herberger* is essentially identical with that devised by *Traill*.

Traill states that his ink was at once adopted (1840) by the National Bank of Scotland, which had recently been the victim of numerous forgeries, in which the ink on bills, &c., had been erased and other figures substituted. As a matter of interest we made inquiries from the present authorities of that bank in Edinburgh, who have kindly informed us that they have no record of any other ink than ordinary iron gall ink having been used by them. It is not improbable that the use of *Traill's* carbon ink was discarded on the introduction of cheques printed with special inks, which would change colour if any chemical were used to remove the writing.

Baudrimont's Soluble Glass Ink.[†]—This is an intimate mixture of soluble glass (sodium silicate) with 10 per cent. of lamp-black. The silica, on separating from the ink during the drying, encloses particles of carbon, thus rendering the characters permanent. It is advantageous to remove the sodium carbonate formed by the action of the carbon dioxide in the air upon the sodium oxide by first treating the written paper with dilute acetic acid, and then thoroughly washing it with water.

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[*] *Trans. Roy. Soc. Edin.*, 1840, xiv. 426.

[†] Desmarest, *Les Encres et Cirages*, p. 144.

We have found that the ink thus prepared from commercial sodium silicate is much too thick for use, and requires to be suitably diluted with water. Ink having a specific gravity of 1.270 flows freely from the pen and gives very black writing. When the dried characters are treated with water the surface ink is readily washed off, but there still remains a greyish writing within the fibres of the paper, and this is not removed by leaving it in water for twenty-four hours. If the writing be left for twelve hours before immersion in water much less of the pigment is removed. The ink can be blotted immediately after writing without rendering it too pale. It is not affected by acids, alkalies, or chlorine.

Other Carbon Inks.—Numerous other formulæ have been given for the preparation of inks of this character, but most of them are only later modifications of those described above. Thus, a weak solution of sodium hydroxide is used instead of hydrochloric acid as a medium for Indian ink (*Bönger*); and another ink consists of lamp-black and gum arabic incorporated with a dilute solution of oxalic acid.

This latter ink has not much penetrating power, and the writing can be removed from the paper by careful washing with water.

Whitfield (Eng. Pat., No. 7474; 1837) prepared lamp-black from a mixture of linseed oil, Venice turpentine, and other organic substances, by firing the mass with a hot iron, and collecting the soot in an inverted cone. 1 lb. of this lamp-black was mixed with 1 quart of vinegar 2 galls. of hot water, ¼ lb. of gum, and ¼ lb. of shellac, and the whole boiled for ten minutes. Powdered galls (1 lb.) and logwood chips (2 lbs.) were then introduced, and the ink stirred until cold, and exposed for three weeks to the atmosphere in flat pans.

Safety Papers used with Special Inks.—*Traill* (*loc. cit.*), in the course of his experiments, tested the permanency of the writing produced by different solutions of metallic salts on specially prepared papers. Sheets of unsized paper were soaked in the following different solutions, and then dried: (i) An infusion of galls; (ii) a solution of potassium ferrocyanide; (iii) sodium chloride solution; (iv) sodium phosphate solution; (v) potassium iodide solution; and (vi) potassium bichromate solution.

i. Characters on this paper made with iron sulphate or copper sulphate were readily removed by chlorine, oxalic acid, &c.

ii. *Ferrocyanide Paper.*—Antimony chloride solution gave bright blue characters, which resisted the action of chlorine, but were effaced by ammonia. Iron sulphate gave dark-blue writing, copper sulphate brown characters, and cobalt nitrate deep-brown characters, which resisted the action of alkalies, but were bleached by chlorine.

iii. *Sodium Chloride Paper.*—The characters produced by silver nitrate on this paper were removed by ammonia.

iv. *Sodium Phosphate Paper.*—Acetate of lead produced intense yellow characters.

v. *Metallic iodides* formed in the paper were equally unreliable, as was also the case with chromates.

vi. *Metallic sulphides*, whether precipitated in the paper or added in the form of coloured compounds (lead sulphide) to ordinary inks, were easily bleached by chlorine.

Indigo sulphate was also bleached by chlorine, but when added to an ordinary iron gall ink increased its stability.

Antimony and Cobalt Salts Mixed.—A mixture of cobalt nitrate and antimony chloride ground together and mixed with gum water yielded an ink which gave dark-brown characters on ferrocyanide paper. The writing was weakened, but not destroyed, by acid or alkali; but when soaked alternately in these reagents was completely effaced.

Summarising the behaviour of different reagents on the metallic compounds tried, *Traill* came to the following conclusions: (i) *Chlorine* bleached all with the exception of the blue precipitate formed on adding antimony chloride to potassium ferrocyanide. (ii) *Oxalic acid* completely bleached gall ink, Prussian blue, lead iodide, mercury iodide, lead chromate, and indigo sulphate, though the last offered more resistance. (iii) *Antimony chloride* weakened or destroyed all the metallic characters with the exception of the antimony ink. Indigo, again, offered considerable resistance. (iv) *Caustic alkalies* destroyed all with the exception of the salt formed by adding cobalt nitrate to potassium ferrocyanide.

Patent Permanent Inks.—The addition of finely divided carbon to ordinary writing inks has been claimed in numerous patents; *e.g.*, by *Scott* in Eng. Pat., No. 8770, of 1840, who added gas-black, indigo and Prussian blue to gall and logwood ink. In *Reade's* patent, No. 11,474, of 1846, the use of Prussian blue was also claimed.

An indelible ink patented by *Stephens* and *Nash* in 1837 (Eng. Pat., No. 7342) was prepared by distributing the carbon in a solution of a resinous soap; whilst *Melville* (Eng. Pat. 534; 1860) claimed an ink consisting of plumbago. with resin, gum, alum, and a suitable colouring-matter. In 1861 *Stevens* (Eng. Pat. 2972) patented an indelible anti-corrosive ink which consisted of solutions of aniline dyes mixed with finely divided carbon. The ink protected by *Gaffard* (Eng. Pat., No. 1839; 1874) was composed of a mixture of carbon with the solution of an alkali silicate.

A mixture of sugar, aniline black, and soot in logwood extract form the constituents of *Fonseca's* patent ink (Eng. Pat., No. 859; 1883); whilst *Wass* (Eng. Pat., No. 9249; 1885) employs carbonised sugar scum as the source of the carbon. A solution of soap in water or other medium is claimed by *Lichtentag* (Eng. Pat., No. 24,644; 1898) as the liquid part of a carbon ink.

Only a few inks of this class not containing carbon have been patented. *Ellis* (Eng. Pat., No. 2267; 1865) claimed that an indelible ink was produced by precipitating colouring-matters by means of silicic acid, and dissolving the precipitate in a suitable silicate solution. In 1891 *Leech* and *Harrobin* (Eng. Pat., No. 1616) protected a writing fluid consisting of turpentine, asphalt, resin, alum, beeswax, and colouring-matter.

Aluminium-powder with a protective varnish forms the basis of *Blancan's* indelible ink (Eng. Pat., No. 7263; 1893).

Patent Safety Papers.—One of the earliest so-called "safety" papers was that described by *Stevenson* (Eng. Pat., No. 7313; 1837). This consisted of paper impregnated with a solution of manganese chloride and potassium ferrocyanide, and was stated to be stained by any chemical that would remove ink.

Ballande's safety paper was impregnated with mercuric chloride, or a salt of iron or copper, whilst the ink consisted of a solution of sodium thiosulphate with alum, or alkali or alkaline salts, or of other salts (*e.g.*, iodides, sulphocyanides, &c.) capable of forming coloured insoluble compounds within the paper. (Eng. Pats., No. 861, 1859; and 388, 1860).

In 1864 *Baildon* (Eng. Pat., No. 2223) claimed the use of a safety paper from which the colour was discharged by acid in the special ink to be used. A patent on similar lines (No. 6938) was published by *Thacker* in 1895, the paper in this case being coated with colour, which was removed as soon as it came in contact with the ink.

It is interesting to note that the colour of ordinary blue paper such as is used for official and commercial purposes is discharged by dilute mineral acid; and we have good authority for stating that acid was actually in use as a white ink on that kind of paper some years before the date of *Baildon's* patent.

CHAPTER XV.

SYMPATHETIC INKS.

CONTENTS.—History—Various sympathetic inks—Patent sympathetic inks.

History.

THE term *sympathetic ink* is applied to writing fluids which yield characters that remain invisible until heated or treated with some suitable reagent. Such inks appear to have been known in the early days of the Roman Empire, for *Ovid* mentions milk as a suitable liquid, whilst *Pliny* refers to the juice of different plants.

The earliest known chemical sympathetic inks were regarded as acting by magnetism. Thus *Brossonius*, writing in a medical treatise in the early part of the seventeenth century, describes a "magnetic fluid" made from "arseniated liver of sulphur," and only visible when looked at with "eyes of affection." This appears to have been nothing more than an ink of lead acetate, the characters being rendered visible by the action of hydrogen sulphide.

*Borel** also describes these inks, the secret of which he learnt from *Brossonius*, as *aquæ magneticæ e longinquo agentes*, but points out that there is nothing miraculous in their action. They are also alluded to by *Otto Tachen* (1669), who denied that there was anything magnetic in their action, and by numerous later writers.

The name *sympathetic* appears to have been first used by *Le Mort* to describe the lead acetate ink, and the term was subsequently applied to all secret inks of the same kind.

In 1715 *Waitz* discovered the use of solutions of cobalt salts as sympathetic inks, and the French chemist *Hellot* also gave a description of them a few years later.

Historiarum Centuriae, iv. p. 110.

Various Sympathetic Inks.—The change in the colour of characters written with a solution of cobalt chloride is due to the fact that the pink salt loses part of its water of crystallisation when heated to 120° C., forming a blue compound, and that the latter on exposure to the air gradually absorbs water, and regains the pink colour which is nearly invisible on white paper. By the addition of other salts to the cobalt solution—*e.g.*, nickel sulphate—the colour of the heated characters is modified.

Cobalt sulphocyanide solutions give pale red writing, which changes to blue on heating.

The following table gives a list of some of the better known substances used as sympathetic inks:

Colour.	Ink.	Mordant.
Black or brown.	Lead acetate. Mercuric chloride. Galls. Pyrogallol. Silver salt	Hydrogen sulphide. Stannous chloride. Iron sulphate. An alkali. (Action of light).
Blue.	Starch. Cobalt nitrate. Iron sulphate.	Iodine. Oxalic acid. Potassium ferrocyanide.
Yellow.	Copper chloride. Basic lead acetate. Antimony chloride.	(Yellow on heating). Hydriodic acid. Galls.
Green.	Cobalt chloride with a nickel salt. Potassium arsenate.	(Action of heat). Copper nitrate.
Purple.	Gold chloride.	Stannous chloride.
Gold.	Gold sodium chloride.	Oxalic acid (10 per cent.) On treating with hot iron metallic lustre is produced.

A sympathetic method might be based on a process familiar to photographers, by which so-called "magic pictures" have been produced. A photographic print on bromide paper after being bleached in a solution of mercuric chloride and thus rendered invisible, is again made apparent by being placed in contact with blotting paper moistened with a solution of sodium thiosulphate ("hypo"). It is obvious that writing executed with any suitable developer on bromide paper would appear and disappear under similar conditions.

Another method is suggested by the fluorescence of a solution of a quinine salt under ultra-violet light, or of other compounds under the influence of radium, X-rays, &c.

Sympathetic inks have frequently been put to an ingenious and perverted use by sharpers of the racecourse, two of whom were recently convicted of this kind of fraud. A betting paper giving the names of horses, &c., is written in two kinds of ink, one of which fades away, whilst the other gradually appears. The disappearing ink commonly used is a weak solution of starch tinged with a little tincture of iodine, and writing done with this soon fades away, whether exposed to the light or not.

The ink used for the invisible writing is often an ammoniacal solution of silver nitrate, which gradually darkens under the influence of light. Fugitive dyes have also been used as disappearing inks, such as—*e.g.*, quinoline blue and furfur-aniline, the solution of which gives magenta writing, which soon fades away under the influence of sunlight.

Patent Sympathetic Inks.—Although sympathetic inks are usually regarded as only scientific toys, they have been applied to several practical purposes, and have been made the subject of different patents.

In the Eng. Pat., No. 2389 of 1877, *Kromer* describes a process for detecting any tampering with envelopes, which consists of separating the two constituents of a sympathetic ink by the adhesive gum, so that should steam be applied to open the envelope, the two substances come in contact and form an ink leaving a stain upon the paper. A similar device was patented by *Pulford* (Eng. Pat., No. 15565; 1889).

Claim is made for the use of bichromate solution in Eng. Pat., No. 3657 of 1881, the characters being made visible by the action of light.

Quelch (Eng. Pat., No. 7472; 1888) has protected a method of writing with a saturated solution of potassium nitrate on a non-glazed surface, a part of the writing being afterwards touched with a red-hot wire. Papers thus treated are sold as toys for children.

A sympathetic ink claimed by *Himly* (Eng. Pat., No. 730; 1887) consists of a solution of platinum magnesium cyanide with a suitable medium, such as gum, gelatin, &c. When exposed to damp air this changes to pink, the colour disappearing on applying heat.

An invisible ink claimed by *Tschofen* (Eng. Pat., No. 2130; 1890) consists of a mixture of chalk or similar substance with water, which is used for writing on a glazed surface, the characters being subsequently dusted over with graphite, bronze powder, &c., to render them visible.

Adams (Eng. Pat., No. 3459; 1896) has patented the use of dilute sulphuric acid (1 : 17) as an invisible ink, the writing being rendered permanently visible on heating the paper so as to bring about surface carbonisation.

Another sympathetic ink which only becomes visible on heating the paper is described by *Moller* in Eng. Pat., No. 21,991; 1897. It consists of about 100 parts of alum and 100 parts of white garlic juice. The writing is rendered visible by heating the paper and cannot be removed by water.

In *Kretschmann's* patent (No. 6727, 1899) paper is treated with a solution of cobalt chloride, and a solution of rock-salt used as ink. On heating the paper the writing appears in pale green characters. In order to detect tampering certain signs are made on the paper with a solution of resorcin and paratoluidine, and these on heating change from red or yellow and become permanently black or brown. In a subsequent patent (No. 7367; 1900) *Kretschmann* has claimed a process of treating paper with a non-hygroscopic salt of cobalt (such as the basic carbonate), and writing on it with a solution of salt and a substance such as vinegar, which will convert the salt in the paper into a hygroscopic salt.

The sympathetic process described by *Buchey* (Eng. Pat., No. 8976; 1899) consists of the use of two substances, such as cobalt chloride and magnesium platino-cyanide, in two layers, one of which becomes visible on heating, whilst the other simultaneously disappears.

CHAPTER XVI.

INKS FOR MISCELLANEOUS PURPOSES.

CONTENTS.—**Ink powders and tablets**—Logwood ink powders—Aniline ink powders—Patent ink powders and dried inks—**Stencil inks**—Show-card ink—**Inks for rubber stamps**—**Inks for writing on glass**—Hydrofluoric inks—Resin inks—Foertsch's pencil for glass—**Inks for writing on metals**—**Ink for writing on leather**—**Ink for ivory surfaces**—**Ink for writing on wood**—**Fireproof inks.**

INK POWDERS AND TABLETS.

THE earliest methods of preparing a powder which would yield an ink on the addition of water consisted of mixing together the finely-powdered ingredients of the ink. Thus *Canneparius*[*] in 1660 describes an ink powder containing equal parts of finely powdered galls and ferrous sulphate, with a sufficient quantity of gum and shellac. Obviously, ink thus prepared would be very pale and of poor quality.

A later method was to evaporate a good iron gall ink to dryness, and to mix the powdered residue with water as required. The disadvantage of this process is that the pigment is rendered insoluble by the evaporation, and that the ink prepared again from the powder contains particles suspended in water instead of being in solution. This objection also applies to *Leonhardi's*[†] ink tablets, which were prepared in a similar fashion.

Dieterich uses his oxidised tannin extract (p. 96) as the basis of portable gall ink powders.

Logwood Ink Powders.—An old Austrian patent taken out by *Platzer*[‡] claimed the use of a powdered ink, consisting of 100 parts of logwood extract with 1 part of potassium bichromate and 10 parts of sodium sulphindigotate.

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[*] *De Atramentis*, 1660, p. 273.

[†] *Dingl. Polyt. Journ.*, 1856, cxlii. 446.

[‡] *Ibid.*, 1859, cliv. 158.

Cooley (Eng. Pat., No. 106; 1867) made claim for ink powders yielding ink of different shades and containing logwood extract or hæmatoxylin with various salts. Thus powdered logwood extract with potassium chromate and bichromate yields an ink of different shades of brown, whilst by adding potassium carbonate to the chromate a rich blue-black ink is produced, the colour being further modified by the addition of alum. The use of copper acetate in place of alum gives a blue-black shade; whilst by using tin chloride, chrome alum or manganese sulphate in place of potassium chromate various shades of purple are produced.

*Dieterich** gives the following directions for making logwood ink powders:

Red Logwood Ink.—Logwood extract, 100; aluminium sulphate, 40; potassium oxalate, 40; potassium bichromate, 3; and salicylic acid, 1·5 parts, in 1 litre of water.

Violet Logwood Ink.—Logwood extract, 100; aluminium sulphate, 40; potassium oxalate, 60; potassium bisulphate, 10; potassium chromate, 5; and salicylic acid, 1.5 parts.

Aniline Ink Powders.—Owing to the readiness with which they dissolve in water, certain aniline dye-stuffs are particularly suitable for the purpose of ink powders.

Viedt in 1875 recommended the use of nigrosine, which was to be dissolved before use in 80 parts of water; and since then aniline dye-stuffs have formed the basis of numerous English patents (*vide infra*).

Dieterich (*loc. cit.*) has also described ink powders of different colours prepared from aniline dye-stuffs:

Black Ink Powder.—Aniline green D., 9; Ponceau R.R., 8.0; phenol blue, 1.

Red Ink Powder.—Ponceau red, R.R.

Green Ink Powder.—Aniline green.

Violet Ink Powder.—Phenol blue, 1.5; Ponceau R.R., 2.0 parts.

Blue-green. Phenol, blue 1.5; aniline green, 2.5 parts.

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* *loc. cit.*

For copying ink powders greater proportions of colouring-matters to water must be used and sugar added, *e.g.*:

Violet Copying Ink Powder.—Methyl violet, 20; sugar, 10; and oxalic acid, 2 parts.

Red Copying Ink Powder.—Eosine, 15; and sugar, 30 parts.

Blue Copying Ink Powder.—Resorcin blue, 5; sugar, 20; and oxalic acid, 1.0 parts.

Patent Ink Powders and Dried Inks.—The earliest patent for an ink powder was taken out by Holman in 1668 (No. 258), but no details of the method of preparing the substance are given. After that date no patent seems to have been applied for until 1867, when *Cooley* (Eng. Pat., No. 106) claimed the use of various dry extracts of dye-stuffs and salts, such as extract of Brazil wood with salts of tin, alum, tartrate, alkali or acid; Prussian blue, soluble indigo with suitable mordant; sap green, with or without alum; saffron with alkali carbonate; extract of French berries with alum; and powdered galls or pyrogallol or a mixture of these with ferrous sulphate.

Byford's Ink Powder (Eng. Pat., No. 974; 1876) contained logwood extract, indigo sulphate, and ferrous sulphate.

In 1878 *Jacobsohn* (Eng. Pat., No. 1586, *Prov.*) described an ink powder for copying, which consisted of a solution of an aniline dye-stuff, with sugar, gum arabic, and glucose evaporated to dryness.

Payne's tablet for inking rubber stamps (Eng. Pat., No. 3179; 1886) consists of glycerin, gelatin, or other glutinous substance, with an aniline or other dye-stuff. An ink in dry form protected by *Ashton* (Eng. Pat., No. 14,388; 1889) is prepared by drying a solution of a soluble colouring containing gum, &c., on wood shaving, gelatin, &c.; and similar patents were granted to *Nienstadt* and *Goldmark* in 1894 for the process of coating granules of non-porous material with a pigment and binding material (Nos. 3236 and 5078). The ink claimed by *Spence* (Eng. Pat., No. 21,830; 1897) consists of an aniline dye-stuff mixed with sodium bicarbonate and a dry acid, the object of the latter being to cause effervescence and thus distribute the pigment through the water.

STENCIL INKS.

Inks intended for use with stencil plates require to be fairly fluid, and to yield characters which dry rapidly, and are not easily effaced.

Blue Stencil Ink.—A mixture of 2 parts of shellac and 2 parts of borax is boiled with water (say 25 parts), and the solution mixed with a sufficient quantity of ultramarine to give the desired colour.

Black Stencil Inks.—(i) The shellac and borax solution described above is mixed with a suitable proportion of lamp-black or nigrosine instead of ultramarine.

(ii) A mixture of 2 parts of manganese sulphate with 1 part of lamp-black and 4 parts of sugar is ground to a paste with a small quantity of water, and a little gum arabic added to give consistency.

Show Card Ink. An ink of similar character to the preceding inks has been recommended for marking show cards and tickets for shop windows. It consists of 16 parts of asphaltum, 18 parts of Venice turpentine, 4 parts of lamp-black, and 40 parts of turpentine oil, thoroughly mixed together.

INKS FOR RUBBER STAMPS.

Many of the inks used with rubber stamps consist of an aniline dye-stuff in a suitable fluid medium.

Black Ink.—This can be prepared from aniline black ½, alcohol 15, and glycerin 15 parts. It is poured upon the cushion of the stamp, and rubbed with a brush.

Blue Ink.—Soluble aniline blue, 3; distilled water, 10; acetic acid, 10; alcohol, 10; and glycerin, 70 parts. The blue is mixed with the water in a mortar, the glycerin then gradually added, and lastly the other ingredients.

Inks of other colours are prepared in the same way, other dye-stuffs being used in place of the blue. For example, methyl violet, 3 parts; fuchsine, 2 parts; methyl green, 4 parts; nigrosine (blue black), 4 parts, &c.

A bright red ink can be obtained by using eosine, but in this case the acetic acid must be omitted.

Reissig's Cancelling Ink.—An indelible ink intended for use with rubber stamps has been devised by *Reissig.* It consists of the following ingredients: linseed oil varnish, 16; fine lamp-black, 6; and ferric chloride, 2 to 5 parts. This ink must not be used with metal stamps.

INKS FOR WRITING ON GLASS.

Hydrofluoric Inks.—One of the simplest fluids used for marking glass is a dilute solution of hydrofluoric acid, which reacts with the silica in the glass, forming a permanent etching.

The objections to the use of free hydrofluoric acid are that it is unpleasant to handle, and that it must be kept in a bottle composed of material—*e.g.*, gutta-percha—upon which it does not act.

It is far better to use a solution of a fluoride which is only mixed with an acid solution when required, as in the case of the following preparation:

Solution I.—Sodium fluoride, 36 parts; potassium sulphate, 7 parts; distilled water, 500 parts.

Solution II.—Zinc chloride, 14 parts; hydrochloric acid, 65 parts; water, 500 parts.

Equal parts of the two solutions are mixed, and the writing done with a clean quill pen. The etching in the glass appears after about thirty minutes.

Resin Inks.—An ink which gives writing not removed from glass by water is prepared by mixing together the following substances: Turpentine, 15; shellac, 10; Venice turpentine, 3; and lamp-black, 3 parts.

Another formula for a fluid for writing on glass is as follows: Rosin, 20; alcohol, 150; borax, 35; methylene blue, 1; and water, 250 parts.

Foertsch's Pencil for Glass.—Eight parts of white wax are fused with 2 parts of tallow, and a pigment such as lamp-black or Prussian blue stirred in while the mixture cools. When nearly cold, it is rolled into pencil form on a slab, and covered with a paper case.

INKS FOR WRITING ON METALS.

Inks for Metals in General.—A black ink which can be used for writing on clean metallic surfaces is obtained by fusing 5 parts of copal, then cautiously adding 6 parts of turpentine oil, little by little, and finally stirring 1 part of lamp-black into the mixture.

For a red ink ½ part of cinnabar is used in place of the lamp-black, whilst inks of other colours can be prepared by the use of suitable proportions of pigments, such as Prussian blue, aniline dye-stuffs, &c.

These inks should be thinned with turpentine oil to the required degree of consistency.

Ink for Zinc Labels.—An ink intended for writing on the zinc labels attached to plants was devised by *Puscher*.* It consists of 1 part of potassium chlorate and 1 part of copper sulphate, dissolved in 18 parts of water, and thickened with a little gum arabic. The writing is black, and will resist a fairly high temperature.

A blue ink for the same purpose is obtained by dissolving 60 parts of potassium chloride and 120 parts of copper sulphate in 1400 parts of water, and mixing the solution with a solution containing 1 part of soluble aniline blue, and 100 parts of dilute acetic acid in 400 parts of water.

Black Ink for Iron, Zinc, or Brass.—A dull black writing is produced on these metals by an ink of the following composition: Copper sulphate, 5; dilute (5 per cent.) acetic acid, 1; gum, 2; and lamp-black 1 part, mixed with 5 parts of water.

Ink for Copper or Tin.—For these metals the ink described in the preceding paragraph must be modified thus: Copper sulphate, 5 parts; ammonium chloride, 3 parts; hydrochloric acid, 3 parts; gum, 2 parts; and lamp-black 1 part, in 5 parts of water.

Ink for Silver.—Yellowish-brown characters are produced on silver by a 7 per cent. solution of the double chloride of gold and sodium, and the colour is changed to black on exposure to the action of light. A solution of platinum chloride can also be employed as a black ink for writing on silver.

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* *Wagner's Jahresber.*, 1873, xix. 206.

INK FOR WRITING ON LEATHER.

The leather is first treated with a 10 per cent. solution of gallotannic acid, containing 1 per cent. of gum arabic, and then dried. It can then be written on with an iron ink of the following composition: Ferrous sulphate, 2; gum, 3; and water 20 parts, to which a little indigo carmine is added to give a temporary colour, pending the formation of the iron gallotannate in the leather.

INK FOR IVORY SURFACES.

*Lehner** recommends the use of solutions of silver nitrate ranging in strength from 10 to 1 per cent., according to the depth of tint required. The ivory is prepared by being immersed in a strong solution of ammonia, and washed with water. The writing may be toned to a brown colour by treatment with a 1 per cent. solution of sodium gold chloride, and fixed in a 10 per cent. solution of sodium thiosulphate (hypo).

INK FOR WRITING ON WOOD.†

The surface of the wood is repeatedly brushed with a boiling solution of gelatin, and then sponged with a mordant containing 10 parts of alum, 2 parts of hydrochloric acid, and 10 parts of tin chloride in 50 parts of water. Writing of different colours may then be done on this prepared surface with solutions of various pigments, such as cochineal (red), decoction of Persian berries (yellow), decoction of anacardium seeds (black), potassium permanganate (brown), decoction of logwood (blue), &c.

FIREPROOF INKS.

Numerous inks have been described which, when used with a specially prepared paper, produce writing that resists the action of fire. Speaking generally, these contain some incombustible material, such as graphite or a metallic compound, which leaves a residue of oxide or metal when heated, and are used with a paper containing more or less asbestos fibre.

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* *Die Tinten-Fabrikation*, p. 128.

† *Ibid.*

The use of such paper with a plumbago ink was claimed by *Halfpenny* in 1873 (Eng. Pat., No. 262), whilst *Hyatt* (Eng. Pat., No. 3684; 1873) also claimed the addition of asbestos to the raw material of paper.

In 1881 *Meihé* patented (Eng. Pat., No. 3410) fireproof inks for writing or printing on paper containing asbestos and wood fibre. These inks contained 5 or 10 per cent. of platinum chloride.

Meihé's Writing Ink.—Platinum chloride, 5; lavender oil, 15; Indian ink, 15; gum arabic, 1; and water, 64 parts.

Fireproof Graphite Ink.—Graphite, 85; copal varnish, 0.08; ferrous sulphate, 7.5; and tincture of galls 30 parts, with sufficient indigo carmine to give the required bluish colour.

Fireproof Paper.—Wood fibre, 1 part; asbestos, 2 parts; borax, 0.1 part; and alum, 0.2 part.

SECTION II.

PRINTING INKS.

CHAPTER VIII.

EARLY METHODS OF MANUFACTURE.

CONTENTS.—Historical—China—Greece and Rome—England—Early printed books—Early methods of manufacture—Fertel's method of making ink—Breton's method—Savage's method of manufacture—Modern methods of preparing ink.

Historical.—*China.*—A work which is said to have been written during the reign of *Wu Wang*, about 1200 B.C., makes mention of the blackening of engraved characters, but it does not seem to be clear whether this refers to inscriptions on stone which would be thus rendered more legible—a method still in use by monumental masons—or to blocks to be afterwards used to yield impressions upon another surface. It seems certain, however, that a primitive mode of printing was known by the Chinese as early as 50 B.C., but that not much advance was made until the reign of *Ming-Tsung*, 927 A.D., when certain volumes were printed from stone blocks for the Imperial College at Pekin. In this early example of the printer's art the characters were cut into the surface of the stone, so that when printed they would appear as white on a black ground. Shortly afterwards engraved blocks of wood, with the letters in relief, were used for another edition of the same work. In the eleventh century an ingenious Chinese block was made, with cut or moulded characters in cubes of porcelain, and these, after being baked to harden them, were pressed into a block of cement so that they could be printed from. The method was not followed up.

The adoption of movable types in China was rendered difficult for the reason that in the Chinese language the words cannot be resolved into the letters of an alphabet. Each word requires a separate character, and as there are about 80,000 of them, of which, however, only 14,000 to 15,000 are in common use, the Chinese printer must be a man of exceptional agility. Nevertheless, a large number of books and periodicals are now printed in China. It is obvious that the Chinese had only to add varnish to the black pigment familiar to them in order to compound a good printing ink.

Greece and Rome.—Although both the Greeks and Romans were acquainted with the art of engraving on metals at a very early period, there is no trace of any attempt being made to transfer designs so cut to other substances, if we except certain stamps which were employed to mark bricks and articles of pottery. There was no inducement to stimulating invention in this direction while slave labour could be employed for writing documents, and we can easily imagine that with the decline of Rome literature would only be cultivated by the very few. But as soon as paper began to be known, and was recognised as a unique material for epistolary correspondence, and for the making of books, the minds of many must have instinctively turned to the possibility of multiplying copies by an engraved surface, and an impression-giving medium.

England.—Caxton came to England and set up a press in Westminster about A.D. 1477 (the exact date has not been ascertainable), but the first paper mill was not established in England until 1498. The printing press was therefore ready nearly twenty years before the means existed in this country of supplying it with its first requisite. But in Italy and Germany paper mills were at work in the thirteenth century, and in France, Switzerland, and Austria in the fourteenth. The arts of printing and papermaking naturally reacted upon one another for the advantage of each, and the Chinese are believed to be the first nation which benefited by their partnership.

Early Printed Books.—Many examples of early printing can be seen in the galleries of the British Museum; and it is interesting to examine the specimens displayed in cases in the King's library there, if only to note the manner in which they have, with very few exceptions, preserved their pristine appearance.

Block Books.—Beginning with the block books, *i.e.*, books in which both cuts and letterpress were cut on solid wood blocks, we find that the earliest bears the date 1470, and we learn from the catalogue that "the long-accepted belief that letter-printing from the solid block was necessarily prior to that from movable types, and must therefore have been introduced by about 1440, is now seriously challenged."

The block book was only used for works of a popular character, and answered the purpose of the modern stereotype block from which a number of copies can be printed without the necessity of resetting type. These early books were presumably printed without the help of a press, the impression being obtained by rubbing the back of the sheet while it was in contact with the thinly inked block. Only one side of the paper was printed, the other being left blank. In later examples, however, both sides of the paper were printed on, and it is interesting to note that the ink penetrated sufficiently into the substance of the paper as to be distinctly seen through as the page lies open in its present situation.

In Case I., which is devoted to these block books, the first example exhibited, the product of an unknown printer in the Netherlands, shows that an ink has been employed which was either brown in colour originally, or has faded to that hue. The more probable explanation is that the ink was made of an impure carbon, which would give a brown tint. In all the other examples in the same case the printing ink is of a full black, although instances are not wanting in which for lack of liberality on the part of the printer it does not present a complete opacity.

These early works follow the old manuscript model in the possession of large ornamental initials, and other adornments which were afterwards added by the "rubricator." In one specimen we can note that the capital letter at the commencement of every sentence has an upright stroke of red, which has as obviously been executed by hand as has been the rough colouring of some of the picture blocks. The specimen referred to is known as the 42-line Bible, which is attributed to the press of Gutenberg at Mainz, about 1455. The red colour has apparently much deteriorated, and it would be interesting to know the nature of the pigment. In another example, the 36-line Bible, also from Mainz, the red initials show a full scarlet.

German Books.—In Case V., which is devoted to examples of early printing from Germany, we find the first illustrated edition of Virgil, 1502 A.D., with a preface in which the compiler boasts in Latin verse that by the help of the pictures the ignorant will be able to follow the text as well as the learned. The illustrations are certainly very good, with engraved lines of such fineness that they must have required an ink of fair quality to do them justice. There is no trace of fading in any of these books, nor should we expect to find any. For carbon is imperishable except by the agency of fire, and, happily, as it is the most easily obtained and cheapest black pigment known, it was naturally adopted by the first printers.

In some cases the ink is seen to have "set off" on the opposite page, a fault from which modern books are by no means free, showing that the varnish used with the carbon was improperly prepared, or that an impure form of lamp-black was used.

Italian Books.—In Case VI., Italy, 1465-1472 A.D., we find specimens of printing which are very brown in tone. In one example, especially No. 7, there are two full-page line drawings (wood blocks), which appear as if printed in strong vandyke brown. The engravings on the hidden side of the leaves are seen through the paper so distinctly as to give the idea that the ink must have contained some corrosive principle that allowed it to eat into the fibres of the paper.

Dutch Books.—In Case IX., Netherlands, there is a specimen with brown ink which compares unfavourably with the brilliant black of the ink in other exhibits in close proximity to it. Another specimen shows the paper yellow and soiled, while the print is strong. In this example there are some marginal notes in a very much faded writing ink. It is quite possible that the brown tint observable in some of these old specimens of the printer's art is due to the use of carbon prepared from the soot of burning wood, or peat. Such a product has long been in use as a brown pigment by water-colour painters under the name of Bistre.

EARLY METHODS OF MANUFACTURE.

The old wall ink (*atramentum tectorium*) described by *Pliny* is the forerunner of our printing ink, which is essentially a kind of rapidly drying black paint.

One of the earliest printed accounts we possess of the manufacture of printing ink is that given by the Venetian *Canneparius** in his book on inks published in 1660. His ink consisted of 1 lb. of a varnish of linseed oil and juniper gum thoroughly incorporated with 1 oz. of smoke-black, and boiled over a slow fire to the required degree of consistency.

According to the description given by *Moxon* in his *Mechanick Exercises*† in 1683, the printing ink then made in England was very inferior to the Dutch ink. The main differences were that in the latter only linseed oil and little rosin were used, that the oil was better prepared, and that the varnish was only incorporated with the black by the pressmen immediately before use; whereas in the manufacture of the English ink much rosin (and frequently train oil) was added to the linseed oil, which was also insufficiently boiled, so that the ink was oily and separated in the paper.

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* *De Atramentis*, p. 260.

† *Moxon's* actual words are worth quoting, if only on account of their quaintness.—"The providing of a good inck, or rather good varnish for inck, is none of the least incumbent cares upon our master-printer, though custom has almost made it so here in England; for the process of making inck being as both laborious to the body, as noysom and ungrateful to the sence, and by several odd accidents dangerous of firing the place it is made in, our English master-printers do generally discharge themselves of that trouble; and instead of having good inck, content themselves that they pay an inck maker for good inck, which may yet be better or worse according to the conscience of the inck maker."

Manufacture of Dutch Printing Ink Varnish.—A cauldron was half filled with old linseed oil, covered, and heated over a brisk fire until the oil boiled. When heated to a sufficient temperature the oil was fired several times, being each time extinguished by means of the cover until eventually a varnish of the required consistency was obtained, this point being determined by cooling a few drops on an oyster shell and testing it between the finger and thumb. It was then allowed to cool somewhat, and clarified by squeezing it in the hand through linen.

When rosin was added, it was used in the proportion of ½ to 1 lb. to each gallon of oil. *Moxon* asserted that the addition of too much rosin made the ink become yellow: but *Savage* denied this, since in his experience rosin thickened the oil, and prevented it separating from the ink and spreading through the paper.*

Moxon stated that suitable varnish might be made without actually *burning* the oil; but here again *Savage's* experience was that, although when linseed oil was boiled until viscous it yielded a clean and workable ink, yet after a few days the oil separated to some extent and spread through the paper.

Savage considered that whilst *Moxon's* strictures on the English press work of the seventeenth century were justifiable, yet compared with the English ink of the early nineteenth century this boasted Dutch ink would have been regarded as worthless.

Fertel's Method of Preparing Ink.—*Fertel*, a French printer of St. Omers, published a work on pressmanship in 1723, in which he described the manufacture of printing ink.†

This was prepared by heating linseed or nut oil in a pot with an adjustable cover until the vapours became inflammable (about 2½ hours), a crust of bread being introduced to "withdraw grease from the oil," and removed when carbonised. The oil was then withdrawn from the fire, the pot uncovered, and the vapours allowed to burn. The addition of turpentine oil advocated by some printers was objected to by *Fertel* on the ground of making the ink clog the face of the type.

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* *The Preparation of Printing Ink.* 1823, p. 29.

† *La Science pratique de l'Imprimerie.* St. Omers. 1723.

The varnish thus prepared was incorporated with smoke-black from pitch resin collected in a chamber hung with sheep-skins, the usual proportions being 5 oz. to 2 lbs. of varnish, and the ink ground thoroughly and worked upon the inking-table. In *Savage's* opinion this proportion of lamp-black was too small for a good ink.

Breton's Method.—In 1751 *Breton*,[*] printer to the King of France, published an account of a very similar method of preparing printing ink. For the manufacture of 100 lbs. of varnish 110 to 112 lbs. of nut oil were heated in a closed copper or iron vessel, which was usually pear-shaped, on a clear fire for about two hours. It was then removed and "burnt," the process being repeated several times. Finally, it was boiled over a slower fire for three hours until of the consistency of glue, when it was strained through linen. Turpentine oil and litharge were not recommended by *Breton* on the ground of their clogging the type.

This "burnt oil" or varnish was thoroughly incorporated by the pressman on the inking-table, with lamp-black in the proportion of 2½ oz. to 1 lb.

Breton's recipe has become a standard one, and was copied into the books of different later writers, such as *Lewis* (1763), *Papillon*, &c.

The method of boiling was substantially identical with the Dutch method described by *Moxon*. *Savage* endorses *Breton's* condemnation of the use of litharge in the preparation of the varnish.

The sixth edition of the *Encyclopædia Britannica* (1823) was apparently the first to publish any substantial difference from these early methods in the manufacture of printing ink, the improvement being the addition of soap to the constituents, an addition which, though probably well known to certain manufacturers, had been kept as a trade secret. The effect of the soap was to cause the ink to leave a clean and sharp impression on the paper, to prevent the type from becoming clogged, and to prevent the ink from "skinning" when kept.

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[*] *Encyclopédie Methodique*, vol. 8, p. 633.

In the *Encyclopædia* recipe the burnt oil was mixed whilst still warm with 2 lbs. of black rosin and 1 lb. of hard soap in slices. In *Savage's* opinion this amount of soap is too much, and would be liable to make the ink daub the type and produce blurred impressions.

Savage's Method of Manufacture.—In 1823 *Savage*, who had studied the manufacture of printing ink from the point of view of the practical printer, published a book on the subject, in which he discussed all the previous methods of manufacture.

For the preparation of the varnish he recommended the use of old linseed oil and black or amber rosin, which was melted into the oil at a temperature of not less than 306° F., the approximate melting-point of the rosin.

Six quarts of linseed oil were heated in a pot over a brisk fire, and the vapours tested with a light from time to time. When the flashes produced became stronger, the pot was removed, and the oil fired whilst kept continually stirred with an iron ladle. The flame was extinguished occasionally by placing the cover over the pot, so as to test the consistency. When, on cooling, it could be drawn into strings about half an inch in length, it was judged to be sufficiently burnt for book-work.

Care was taken to prevent the oil frothing up through too violent heating, and thus running the risk of the entire mass bursting into uncontrollable flame.

After cooling somewhat in the covered vessel the "burnt" oil was mixed with 6 lbs. of rosin gradually stirred in, and then with 1¾ lbs. of brown soap in thin slices, and was finally heated to the boiling-point.

This varnish, whilst still warm, was next poured little by little into an earthenware vessel containing 5 oz. of Prussian blue or indigo, or a mixture of these, 4 lbs. of mineral lamp-black, and 3½ lbs. of vegetable black, and the whole stirred until free from lumps, and finally ground in a levigating mill.

Modern Methods of Preparing Printers' Ink.—Although the old method of preparing printers' or lithographic varnish, by heating the linseed oil until inflammable vapours are given off, and setting fire to these, is still in use, it has been found that the actual burning of the oil is not an indispensable part of the process, and various other methods of thickening the oil and converting it into varnish are now employed.

Other ingredients are also added to the linseed oil varnish in addition to the rosin and soap used in *Savage's* time, and this is especially the case with the cheaper kinds of inks such as are used for newspaper work. Various processes for preparing a black pigment to be used in place of lamp-black have also been described in patents taken out during the last thirty years.

CHAPTER IX.

MANUFACTURE OF VARNISH.

CONTENTS. Boiled oils—Paint oil—Varieties of lithographic varnish—Andre's apparatus for boiling oil—Apparatus with steam jacket and air blast—Boiling with superheated steam—Treatment with oxygen—Linseed oil substitute.

Boiled Oils.—The oils classified under the term "drying oils" are distinguished from other oils by the greater rapidity with which they form a solid varnish on exposure to the air at the ordinary temperature. Strictly speaking, this difference is one of degree rather than of kind, for it has been shown that even oils, such as olive and almond oils, do eventually dry after the lapse of a long time.

The principal drying oils are linseed, walnut, hempseed, poppyseed, nigerseed, and the curious tung, or Chinese wood oil. For the characteristics and methods of examining these oils the reader is referred to works on the analysis of oils. Other oils, such as cotton-seed and maize oils, occupy an intermediate position between the "drying" and "non-drying" oils, and are usually known as "semi-drying" oils. The drying capacity of oils is usually attributed to the presence of a considerable amount of the liquid fatty acids, linolenic and isolinolenic acids, whilst another acid, linolic acid, probably contributes to the process.

Fixed vegetable and animal oils consist in the main of compounds of glycerin with saturated and unsaturated fatty acids, the latter predominating. Thus, olive oil consists principally of a compound of glycerin and oleic acid, $C_{18}H_{34}O_2$; cotton-seed oil contains a large proportion of glycerides containing linolic acid, $C_{18}H_{32}O_2$; whilst linseed oil and other "drying" oils are characterised by the amount of the still more unsaturated linolenic and isolinolenic acids, $C_{18}H_{30}O_2$, they contain.

Each of these unsaturated fatty acids and their glycerin compounds (glycerides) are capable of entering into combination with chlorine, bromine, or iodine, forming saturated compounds. Oleic acid, for instance, yields oleic dibromide, $C_{18}H_{34}Br_2O_2$; linolic acid gives linolic tetrabromide, $C_{18}H_{32}Br_4O_2$; and linolenic acid, linolenic hexabromide, $C_{18}H_{30}Br_6O_2$.

In like manner they are capable of being saturated with oxygen, and this is part of the change that occurs when a film of drying oil hardens into a varnish on exposure to the air, whilst the process can be considerably accelerated by subjecting the oil to a preliminary treatment known as "boiling."

In this process, the exact nature of which still needs elucidation, considerable alteration of the "raw" oil takes place during the partial oxidation. Such boiled oils were at one time prepared solely by means of heat, but subsequently various substances, known as "driers," were added to accelerate the oxidation, which was also promoted by injecting hot air into the hot liquid.

Of the various "driers," which appear to act mainly as conveyors of oxygen from the air to the oil, salts of lead and manganese, in the proportion of a few pounds to the ton, have been found the most satisfactory, and are the most frequently used.

The varnish used in the manufacture of printers' ink differs from the varnish used by painters and linoleum manufacturers in being prepared without the addition of any "driers" whatever. It is also as a rule much paler in colour.

The apparatus used in the old method of boiling oil consists of a kettle, which is heated over a free fire (Fig. 30). Over this is suspended a lid, which can be lowered to close the vessel and immediately extinguish the flames when the evolved vapours take fire. To prevent frothing, the pan is only filled to half its capacity with oil.

Burnt Oil.—In preparing oil for the manufacture of printing ink, the process of oxidation is carried still further than in the process of boiling. In the old process of firing, as described in the preceding pages, the oil becomes very dark in colour, and apparently undergoes considerable decomposition, probably attended with polymerisation similar to that which occurs in the vulcanisation of oils by means of sulphur chloride.

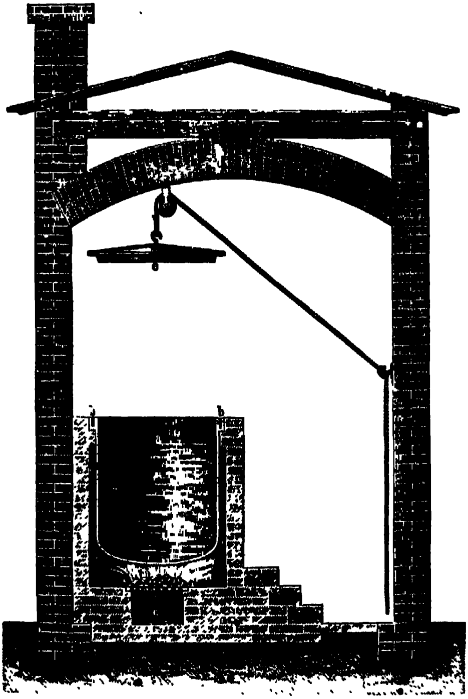

Fig. 30. Free-fired pan for boiling oil.

The amount of free acid liberated in the oil during the process is much greater than in the case of oil that has been boiled for a very long time at a temperature of 260° to 300° C.

Printers' varnish thus prepared has good drying properties, and is considerably denser than the raw oil (*vide infra*)

Leeds[*] gives the following details of the modern method of boiling oil for lithographic varnish: The kettle is filled to about two-thirds of its capacity with linseed oil that has been kept in store for some time. As soon as the water has been expelled and the froth of albuminous impurities skimmed off, the temperature is raised to about 500—560° F., and the boiling continued until the required degree of consistency is attained, after which the varnish is left to cool and settle and decanted into storage tanks.

The time required depends upon the temperature of boiling and on the maturity of the raw linseed oil. A high temperature accelerates the conversion, but has the drawback of producing a darker product.

Leeds lays considerable stress on the importance of using a well-matured oil. Crude linseed oil immediately after expression contains impurities which separate out to a greater or less extent on standing for a few months. If such crude oil be used for boiling there is much more froth and a poorer yield of a darker varnish, whilst the time and consumption of fuel are greater.

The ordinary loss ranges from about 3 to 10 per cent., according to the maturity of the oil.

It is interesting to note that the importance of using an old oil in the preparation of the varnish was recognised by all the older writers from *Moxon* to *Savage*.

Varieties of Lithographic Varnish.— Five or six varieties of lithographic varnish are in use, ranging in consistency from a very thin product to one of extreme viscosity. These are termed, "extra strong," "strong," "middle," "thin," "tint," and "thin tint," according to their degree of viscosity. *Leeds* (*loc. cit.*), who has thoroughly studied the chemical changes that take place in the conversion of the raw oil through the various intermediate changes into "extra strong" varnish, points out that the most viscous products have less drying capacity than the thinner varnishes, and that their viscosity, which gives them greater carrying power as a medium for pigments, is their chief recommendation.

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[*] *Journ. Soc. Chem. Ind.*, 1894, xiii, 203.

The following table, abridged from that of *Leeds*, represents some of the changes undergone by raw linseed oil in this process of boiling, and in the old method of igniting the vapours to produce "burnt" oil.

Varnish	Specific gravity at 15.5° C.	Free acids as oleic acid	Saponification value	Iodine value.	Unsaponifiable matter
		Per cent			Per cent
"Tint" . .	0.9584	1.46	197.5	113.2	—
"Thin" . .	0.9661	1.76	196.9	100.0	0.62
"Middle" . .	0.9721	1.71	197.5	91.6	0.85
"Strong" . .	0.9741	2.16	190.0	86.7	0.79
"Extra strong" .	0.9780	2.51	188.9	83.5	0.91
"Burnt" thin .	0.9675	6.93	195.5	92.7	1.35

Andrés' Apparatus for Boiling Oil.—This (Fig. 31) consists of a cylindrical copper kettle, A, to the middle of which is attached the collar *D*, which supports it in the furnace. The top of the vessel is bound by a strong iron ring, to which are attached the chain and tackle *C*, thus enabling the vessel to be rapidly withdrawn from the fire by means of a crane. The lid, *B*, fits closely to the upper ring, forming a nearly air-tight joint, so that flames can be immediately extinguished. Above the furnace is fixed a hood provided with a flue to conduct away the vapours.

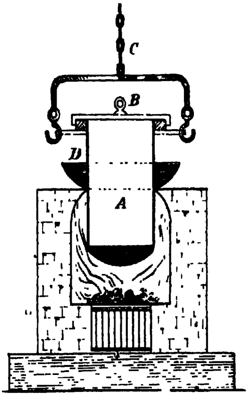

Fig. 31.—Andrés' apparatus.

It was asserted by *Savage*, and accepted for long afterwards, that actual ignition of the vapours from the oil was essential for the production of a varnish suitable for printing ink. It is now known, however, that the same result can be obtained by boiling the oil at a higher temperature than in the preparation of ordinary boiled oil for paints.

Apparatus with Steam Jacket and Air Blast.—A pair of steam-heated kettles, each of which takes a charge of about 350 kilos., is shown in Fig. 32. These are constructed with jackets capable of resisting a pressure of several atmospheres. The oil is heated by steam at about 130 C. or more, under a pressure of four to five atmospheres, whilst air is blown through until the varnish is of the required consistency. Each kettle is covered with a dome-shaped cover, in which is an outlet pipe for the escape of the vapours evolved. The steam enters the jacket of the pan b at c′, and passes through e into the jacket of the pan a. At f is a cock for blowing off, which is so regulated that only a little steam escapes, whilst the condensed water is drawn off through the tap at g.

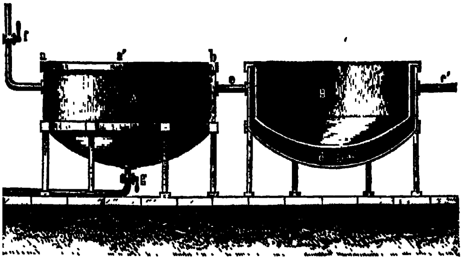

Fig. 32.—Steam-heated kettles.

Frederking's apparatus for boiling oil contains a steam coil, round which has been cast the molten metal forming the pan. Steam under any required pressure is passed through the coil, and the contents of the kettle readily raised to temperatures of 350° to 400° C. without danger, the pressure being solely on the piping and not on the metal pan itself.

An apparatus described by *Andés** contains a circular iron pipe supported on the bottom of the vessel, and connected with bellows by means of a vertical tube. Air is blown into the oil through small holes about 0.5 c.m. in diameter in the circular pipe, and the heated oil kept in motion during the thickening process. When cold air is blown into the oil the temperature is kept below 270° C. to prevent the varnish being too dark in colour.

Sauer's Apparatus.—This consists of a heating vessel in which a paddle agitator is made to revolve round a central shaft, whilst a current of hot air enters near the bottom of the apparatus.

Fig. 33 shows another apparatus for preparing varnish by this method. The air is driven by means of the pump *A*, through the coil *B*, and is heated to the required temperature before entering the oil in the vessel *C*, through the small openings in the pipe.

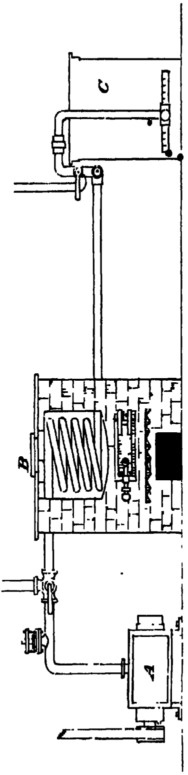

Fig. 33.—Apparatus for hot-air treatment of oils.

The varnish produced by this method dries well, but is usually somewhat darker than that produced by the ordinary method, especially if the temperature be allowed to rise too high.

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* *Drying Oils*, 1901, p. 237.

Boiling with Super-heated Steam.—Apparatus in common use for this purpose consists of a kettle containing a coil through which passes steam heated to a temperature of about 400° C. by being passed through a super-heater kept outside the chamber. The kettle is provided with a cover which can be easily removed by means of a chain and tackle, whilst an exit pipe in this cover conducts the escaping vapours to the bottom of the super-heater, whence they are drawn up into the fire and consumed. Hence the process is accompanied by little or no smell.

Lithographic varnish thus prepared has the drawback of being darker in colour than ordinary "boiled" varnish, but, on the other hand, the process is much more rapid.

Treatment with Oxygen.—Very pale varnishes are obtained by subjecting linseed oil, heated to a moderate temperature, to the action of oxygen. Instead of losing in weight as in the ordinary boiling processes, the varnish shows an increase of about 4 per cent. through the addition of the oxygen.

Leeds (*loc. cit.*) found that varnishes thus prepared were free from the brownish-green fluorescence of ordinary lithographic varnishes, but that they possessed a much more unpleasant odour.

In a process protected by "Brin's Oxygen Co." (Eng. Pats., No. 12,652, 1886; and No. 18,628, 1889) a current of pure (90–93 per cent.) oxygen is passed into the space above the oil, instead of being blown through it. The apparatus used for the purpose consists of a closed steam-jacketed pan, in which the oil is kept in motion by a revolving agitator. The oxygen is introduced when the oil has been heated to nearly 100° C., and is absorbed, at first slowly, and eventually more rapidly than it is supplied. So much heat is produced by the reaction that it is ultimately necessary to cool the jacket by admitting water into it.

Linseed oil varnish prepared by treatment with oxygen differs from the original much more than varnish prepared by boiling. Thus it contains about ten times as much free acid, and has a considerably higher specific gravity, whilst its absorption capacity for iodine is much lower.

Leeds (*loc. cit.*) gives the following results obtained in the analysis of two samples of these oxidised linseed oils.

Varnish.	Specific gravity at 15° C.	Free acids as oleic acid.	Saponification value.	Iodine value.	Unsaponifiable matter.
		Per cent.			Per cent.
Oxidised oil, weak .	1.03	18—28.4	221	58.8	0.87
Oxidised oil, strong .	1.05	18.5—28.9	223.5	53.5	0.97

Treatment with Ozone.—It was shown some years ago by *Schrader* and *Dumcke* that a varnish was rapidly produced by the action of ozone upon raw linseed oil, which was also bleached in the process.

Apparatus for the purpose was subsequently patented in Germany by *Graf and Co.*, a current of ozone from any suitable generator being conducted through the heated oil. Care is needed in this operation to prevent the oxidation proceeding too far, so that a semi-solid caoutchouc-like mass is obtained. In fact, patents for preparing commercial rubber substitutes by the action of ozone under pressure upon linseed and other oils have been taken out by *Rosenblum* and *Rideal* (Eng. Pats., No. 9529, 1897; and No. 6464, 1898).

Ramage (Eng. Pat., No. 7242, 1901) has devised a process for making varnish of good drying capacity by heating non-drying oils with ozone in the presence of an oxygen-occluding substance such as platinised asbestos.

Muthel and Lutke's Electric Process.—In this process, patented in Germany (Ger. Pat., No. 29,961), the oil is treated with a mixture of gases (*e.g.*, oxygen with steam, or nitrous oxide with air or oxygen) which has been subjected to the action of a powerful electric discharge whilst passing through a series of condensers. The oil is heated by means of a steam coil, whilst the gaseous mixture enters through holes in a small spiral in the bottom of the tank. The volatile products of the reaction and the unused gas are drawn off by a pump at the top.

Linseed Oil Substitutes.—Numerous substances have been proposed as substitutes for linseed and other drying oils. An ink containing none of the ordinary oil varnish was described by *Savage* in 1823 (*loc. cit.*), and methods of preparing other varnishes of the same kind can be found by reference to the patent list at the end of this book. One of the most interesting of these is a natural drying mineral oil, which is found in Java and known commercially as Grisel oil. The use of this is claimed by *Sloop* (Eng. Pats. No. 24,504, 1897; 23,071, 1898).

CHAPTER IX.

PREPARATION AND INCORPORATION OF THE PIGMENT.

CONTENTS: Black for printing ink—Modern apparatus—Thenius' lamp-black furnace—Furnace for producing black from pitch—Other black pigments—Carbon blacks—Purification of lamp-black—Composition of lamp-blacks—**Methods of examining lamp-blacks and gas-blacks**—**Mixing the black and varnish**—Mixing the varnish and lamp-black—Quack's mixing machine—Werner and Pfleiderer's mixing machine—Lehmann's mixing machine—**Grinding**—Lehmann's grinding machines—Machines by Neal, Jackson, Kingdon—Lithographic printing ink—Collotype ink.

Black for Printing Ink.—The nature and degree of purity of the black pigment incorporated with the varnish is of the highest importance, especially in the case of ink intended for fine-art printing, since the depth and permanency of the tone largely depend on this. Hence many printing ink manufacturers prepare their own lamp-black so as to have the entire manufacture under their control, and to be able to produce an absolutely uniform product. Some of the older methods and apparatus used in the preparation of lamp-black have already been described in chap. i., and here it is only necessary to describe some of the more modern apparatus.

Fig. 34 represents a modern apparatus used for the production of lamp-black from oil, and is a development of the ancient method. The supply of oil is regulated by the small chamber outside, whilst the air enters through holes beneath the lamp. The smoke from the lamp is conducted through the chimney into a chamber, where it is deposited and collected.

Another apparatus intended for the rapid production of a coarser lamp-black is shown in Fig. 35. It consists of a revolving cylinder, through the interior of which passes a current of cold water. A series of lamps are kept burning below this, and the smoke deposited on the cylinder is removed by means of the brush.

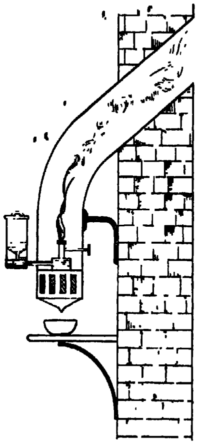

Fig. 34.—Lamp-black apparatus.

Thenius' Lamp-black Furnace—This apparatus, devised by *Thenius* for the collection of lamp-black from coal-tar oil, consists of a series of iron chambers opening into one another. If the first of these the oil, freed from naphthalene as far as possible, falls drop by drop from a tank above on to a red-hot plate, over which passes a limited supply of air. The smoke is carried through the series of chambers, forming black deposits of different grades of fineness on the walls. About 70 kilos. of smoke-black are obtained from 400 kilos. of the oil, about half of it being of very fine quality.

Furnace for producing Black from Pitch, Rosin, &c.—An apparatus used in Germany consists of a chamber with a slanting outlet tube for the smoke leading to the chamber where it is deposited, and a movable iron cover with a regulator for the air supply. The combustible material is placed in a pan at the bottom of the chamber, whilst the exterior of the pan is cooled in another tray containing water, the object of this being to prevent the temperature rising too high and causing dry distillation to take place.

In a recent United States patent (No. 741,726, 1903) tar is heated to about 300°–400° C. in a rotating cylindrical furnace, in which is a spiral ridge to conduct the tarry matter towards the outlet at one end, whilst the volatile products escape through a special opening.

Other Black Pigments.—Numerous substitutes have been proposed for lamp-black as a pigment in printing ink, but not many of these have come into general use.

Frankfort black or *drop black* was originally prepared by heating vine twigs in closed crucibles, extracting the residue with water, drying the powder, mixing it with a weak solution of glue, and forming it into pear-shaped drops. Other substances, such as bone shavings, &c., are now used in its manufacture.

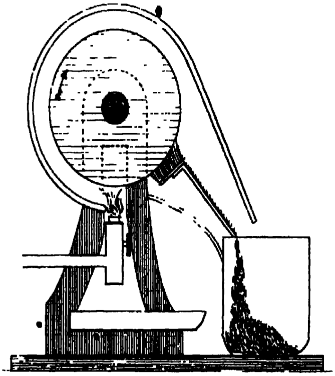

Fig. 35.—Lamp-black apparatus.

This and other forms of charcoal have a granular character, whereas lamp-black is flocculent, and as no amount of grinding will effect thorough incorporation of such granular pigments with the varnish, they are unsuitable for good printing ink. The same remark applies to various shale and mineral blacks.

Carbon Blacks.—The black pigment obtained by the deposition of the smoke from burning gas upon metallic surfaces is sold under various trade names, such as *gas black*, *peerless black*, *hydrocarbon black*, *silicate of carbon*, *jet black*, &c.

It was prepared on a small scale by certain manufacturers in this country from the ordinary gas supply of towns some forty years ago, but owing to its high price (5s. a pound) never came into general use.

The discovery of natural gas in different parts of the United States put a cheap source of gas carbon at the manufacturers' disposal. *Cabot*[1] states that the first experiments with the natural gas were made in 1872 in Pennsylvania, and a factory was built to manufacture the pigment on a commercial scale. The first lot was sold at about 10s. a pound, and the demand soon exceeded the supply. Other factories were established and the price rapidly fell, until in 1889 it was as low as 1½d., and several firms were ruined. Since then it has again risen somewhat in price, and now fetches about 3d. or 4d. a pound, which is dearer than the price of black prepared from the smoke of heavy oils.

The gas issues from borings about 2000 feet in depth by 8 inches in diameter, and is burned in ordinary gas jets. In the earliest method of collecting the black flat-bottomed cast-iron pans were fixed above the jets, and the soot removed by means of travelling scrapers. Several United States patents were next taken out for processes in which the flame was made to impinge on revolving iron cylinders. In 1883 claim was made for a process in which a large plate with holes for ventilation was made to revolve over the burners, and the black removed by passing over a fixed scraper.

The method now in general use was introduced in 1884 by *Blood*, who employed revolving iron rings 3 feet in external diameter and 2 feet in internal diameter as the surface for the deposit. These rings were placed in six rows of fourteen each, and were enclosed in sheds to guard against air draughts.

In another process, also commercially successful, the deposition surface is kept stationary, whilst the gas jets and collecting box revolve beneath it.

The best yields obtained by these processes are about one pound of black for each 1000 cubic feet of gas consumed, but in some cases the consumption of gas is six or eight times as much.

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[1] *Journ. Soc. Chem. Ind.*, 1894, xiii. 128.

Carbon blacks are characterised by their intensity of tone, and the printing done with inks containing them has a rich glossy appearance. Owing to their being of a more granular character than lamp-black they are not so readily incorporated with the varnish, and were not looked upon with favour by English printers long after they had been extensively used in America. English manufacturers have now introduced rollers of chilled steel in place of granite for the grinding of carbon black inks, and their products can compete with those of American origin.*

Gas-black consists mainly of carbon, and has only traces of mineral matter. Samples analysed by *Cabot* (*loc. cit.*) contained 92 to 93 per cent. of carbon, 5 to 6 per cent. of oxygen, and 1 to 2 per cent. of hydrogen.

Like lamp-black, impure gas-black is always contaminated with tarry oils, which can be removed by calcination (p. 156), leaving a residue containing 98 to 99 per cent. of carbon. Its tinctorial power is considerably higher than that of lamp-black, and it will impart a deep grey tone to 100 times its weight of white lead. It requires approximately twice as much varnish as lamp-black does to form an ink of the right consistency, and the ink thus dries more slowly.

Owing to its hygroscopic character, carbon-black must be stored in well-closed vessels, otherwise the water it absorbs forms globules with the oil, and interferes with the perfect incorporation.

Carbon-blacks are miscible with water, and this property affords a means of distinguishing them from lamp-black.

Purification of Lamp-black.—However carefully prepared, lamp-black, even after careful grading, has a more or less brownish tint, due to the presence of volatile, tarry, and oily matters derived from dry distillation of part of the organic substance used in the combustion. When these are eliminated, the residue consists of almost pure carbon, and is then deep black in tone.

Chemical Purification.—The technical method of removing the brown impurities is to boil the black with successive

Harding, *Process Year Book*, 1898, p. 65; 1902, p. 126.

portions of strong caustic soda ley until only a faint colour is imparted on treating the substance with a new portion. The powder is then washed thoroughly and appears deep black to the eye.

In order to remove all traces of impurities, however, it is necessary to continue the boiling with caustic soda until a colourless extract is obtained, and subsequently to boil the residue with *aqua regia* until nothing more dissolves. The final product, after washing with water, is a deep black, very friable powder. It is practically pure carbon, and emits no smell when burnt. The cost of handling the material so many times is too great to permit of chemical purification being used in the preparation of any but the very finest and most expensive grades of lamp-black (*Andés*).

Purification by Calcining.—The brown tarry oils and other impurities in lamp-black can be expelled by heating the crude product to a sufficient temperature to volatilise them. In this process it is essential to prevent any air coming into contact with the hot carbon, which in that case would be partially burned into oxides of carbon; and also to avoid overheating, the result of which is to cause the lamp-black to cake into lumps, which are very difficult to distribute uniformly through the lithographic varnish.

The apparatus used for the calcination is a cast-iron box, in the cover of which a small opening is left to allow the volatile impurities to escape. The outside of this box is coated with a thick layer of clay to protect the metal from oxidation, and the juncture of the cover carefully luted with the same material. Every precaution is taken to avoid the slightest opening into the box, with the exception of the small one in the cover.

After being charged with the crude lamp-black, the box is placed in a suitable furnace and heated gradually from behind until the whole has attained a bright red heat. It is kept at this temperature for about thirty minutes, and then removed from the furnace and cooled in a current of air, the opening in the cover being protected from the possible admission of atmospheric oxygen by having a piece of glowing charcoal placed over it. The box is not opened until quite cold, lest any oxidation of the carbon might take place. To obtain an absolutely black product, it is often necessary to repeat the calcining as many as six times or more. According to *Irvine* the loss in weight on calcining lamp-black is upwards of 15 per cent.

Composition of Lamp-blacks.—After careful purification lamp-blacks consist of 96 to 98 per cent. of carbon, and contain very little mineral or oily products.

The following analyses of four pure samples of lamp-black were made by *Stillwell* and *Gladding**:—

	1 Per cent.	2 Per cent.	3 Per cent.	4 Per cent.
Carbon . .	97.38	97.38	96.21	96.13
Mineral matter (ash) . .	0.05	0.05	0.03	0.23
Moisture (loss at 100° C.) .	0.07	0.08	0.03	0.04
Volatile substances . .	2.50	2.50	3.70	3.60

A commercial sample of impure lamp-black recently examined by us gave the following results:—Ash, 0.29; oily matter (ether extract), 8.12; and total nitrogen, 0.76 per cent.

METHODS OF EXAMINING LAMP-BLACKS AND GAS-BLACKS.

In judging of the suitability of a black for printing ink, the main points to be taken into consideration are the intensity and permanency of its blackness, its tinctorial power, the fineness of its particles, and its freedom from any considerable proportion of oily impurities and mineral matter.

Determination of Mineral Matter.—A weighed quantity (about 0.3 grm.) of the powder is ignited in a weighed platinum basin over a small Argand flame, and the residue weighed when burned completely white. The best qualities of lamp-black contain only traces of ash (*cf.* "Analyses" *supra*).

Tarry Oils.—It has been pointed out by *Irvine*† that the halo to be observed round the letters in some old books

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[*] *Process Year Book*, 1901, p. 141

[†] *Journ. Soc. Chem. Ind.*, 1894, xiii. 131.

and papers is to be attributed to the presence of tarry compounds, such as pyrene and chrysene, in the black.

For the determination of such impurities, 2 or 3 grms. of the sample are extracted with ether, the extract evaporated, and the residue weighed. A specimen of lamp-black examined by us in this way yielded 8.12 per cent of a dark yellow viscid oil, with a strong empyreumatic odour and a bitter taste. *Smith*[*] advocates the following qualitative test:—A pinch of the powder is put on a piece of filter paper and moistened with a few drops of sulphuric ether, which will dissolve any oil present and then leave a brown or yellow stain surrounding the powder.

Alkalinity or Acidity.—Free alkali or acid, which may be left by the process of purification, may react with other constituents of the ink and lead to loss of colour.

Free alkali is detected by boiling 0.1 grm. of the black with 10 c.c. of water, filtering, and adding a drop of phenolphthalein solution to the filtrate (pink colour). If, on the other hand, the aqueous extract is acid, it will remain colourless on the addition of the phenol-phthalein, and will require the addition of alkali solution to produce the pink colour.

Degree of Fineness.—Lamp black consists of foliated particles, while gas-black is finely granular in character, and vegetable charcoals (Frankfort black, &c.) still more granular. A practical test for comparing an unknown sample with one of known fineness is to mix equal weights of the powders with equal quantities of varnish, and to spread the mixtures in thin layers on glass. When the glass is held to a strong light, the layer of fine black will be found impervious to the light, whilst the particles of the coarse black allow the light to pass.

Intensity.—The above method of testing the fineness of the particles is also frequently employed for comparing the intensity of the tone of two samples; but *Smith* (*loc. cit.*) objects to it on the ground that in the case of shale-blacks the oil varnish may rise to the surface, and the layer thus appear to be blacker than it really is. He therefore advocates making the comparative tests on wood instead of glass, under parallel conditions.

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[*] *Process Year Book*, 1903, p. 137

Permanency.—Apart from the results obtained in actual practice which obviously take time, *Smith* recommends testing the blacks with sulphuric acid and with solutions of sodium hydroxide and ammonia. Effervescence with the acid indicates the presence of carbonate, whilst if the blackness is at all fugitive, the pigment, when dried after treatment with alkali, may show a loss in intensity.

Tinctorial Power.—A paste is prepared by adding linseed oil to a mixture of 0.1 grm. of the black with 8 grms. of white lead, and after thorough incorporation spread upon glass, and the tint compared with that given by a standard sample of lamp-black under the same conditions.

Opacity Test for Covering Power.—A mixture of 0.1 grm. of the powder, and 1 c.c. of oil is spread in a uniform layer over paper until the surface below becomes visible, the areas of paper covered by equal weights of two pigments thus affording a measure of their relative opacity. In some cases an additional amount of oil must be added to the mixture to enable it to be spread out to its maximum extent, so that the total amount of oil used may also be taken as a measure of the covering power.

Distinction between Lamp-blacks and Gas-blacks.—*Cabot* (*loc. cit.*) has based a distinguishing test on the fact that gas-black can be readily mixed with water (p. 155).

MIXING THE BLACK AND VARNISH.

Proportion of Black to Varnish.- This will obviously depend to a large extent on the character of the printing for which the ink is required, as well as on the quality and nature of the pigment used. Thus for newspaper work a very different kind of ink is required than in the case of fine book work and illustrations.

According to *Andés*,[*] the proportion of lamp-black or other black in German printing ink ranges from about 20 to 40 per cent., a little blue pigment (indigo, aniline dye-stuffs, &c.) being added to the best qualities of ink.

He gives the following proportions as typical of inks in common use:

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[*] *Oel und Buchdruckfarben*, 1889, p. 236.

	Ink for Rotary Machines.	Common Newspaper Ink.	Book Ink.	Ink for Illustrations.	
	Per cent	Per cent	Per cent.	Per cent.	Per cent
Oil Varnish .	70 72	76 78	77 79	78	78
Lamp-black .	30-28	24 22	23 21	20	19
Paris Blue . .	—	—	—	2	2
Indigo .					1

Mixing the Varnish and Lamp-black.—In some of the old foreign methods of mixing the pigment with the oil varnish, the ink was only incorporated by the pressman on the inking-stone immediately before use (see p. 136). As a thorough admixture of the ink was a tedious process the old English ink manufacturers were in the habit of preparing a complete product, though, according to *Moxon (loc. cit.)*, the results given by this ink were inferior to the Dutch printing. The mixing of the ingredients was effected by stirring them together in a vessel, and eventually grinding them on a stone with a muller. Owing to the very light and dusty nature of the lamp-black, the

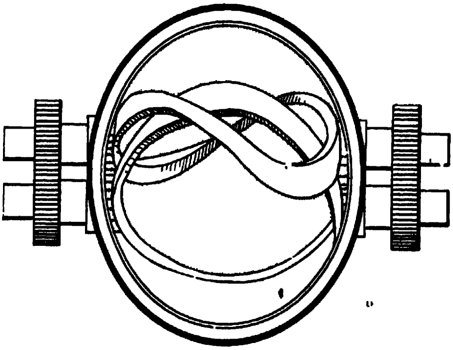

Fig. 36.—Quack's Mixing Machine.

incorporation is now usually effected in a mixing machine, several types of which are in use.

Quack's Mixing Machine.—This is a simple and effective apparatus, consisting of a closed vertical cylinder with rounded bottom, in which revolve two interlapping flat rings, which scrape the sides of the vessel and effect a thorough admixture of the contents. The cylinder is supported outside by axles, so that it can be easily inverted to remove the ink.

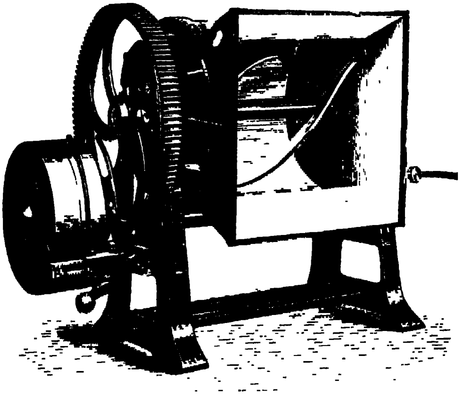

Fig. 37.—Lehmann's Mixing Machine

Fig. 36 shows the mixing apparatus viewed from above.

Werner and Pfleiderer's Mixing Machine.—These are made in various sizes to take charges of ½ to 1400 kilos. They are constructed in the form of a horizontal cylinder, mounted on axles so as to be readily emptied, and the incorporation of the varnish and lamp-black is effected by means of revolving paddles.

Lehmann's Mixing Machine.—Fig. 37 represents the mixing machine supplied by Messrs. *Keller and Co.* for mixing lamp-black with oil. It is made in two sizes to take charges of twenty-two and sixty-six gallons, and the rotating blades are driven by 0.2 and 0.5 horse-power respectively. The machine is shown here in a tilted position for the discharge of ink, but when in action the opening of the vessel is horizontal, and is closed so as to be completely dust proof. A special lamp-black cylinder is attached to the cover of the machine, and the black falls from this through a sliding shutter into the mixing chamber.

GRINDING.

After thorough admixture in a mixing machine as described in the preceding pages, the *pulp* of printing ink requires grinding between rollers, so as to reduce it to an absolutely homogeneous mixture free from all lumps. For this purpose it is transferred from the mixer to a mill, in which it is passed between rollers of fine-grained hard stone such as porphyry, one grinding in a mill with six or nine rollers being usually sufficient if the material has been properly mixed.

For grinding granular pigment such as gas-black, machines with rollers of chilled steel are used in America and more recently in England.

Lehmann's Grinding Machines.—These machines have been extensively supplied by Messrs. *Keller and Co.* to printing ink manufacturers. They are constructed in different sizes and with three hard metal rollers of chilled steel or of porphyry. A mill suitable for smaller manufacturers is shown in Fig. 38. This is 40 inches in length, 47 inches wide and 45 inches high, and has rollers 8 inches in diameter. These rollers are composed of porphyry, and have a surface harder than steel, so that the material is ground as finely as possible. They are made to run at different speeds, whilst the front roller has also an oscillating movement, both of which help to make the grinding more thorough.

Further advantages claimed for this type of mill is that there is no possibility of the material overflowing from the sides, and that the rollers keep completely cool during the grinding, thus preventing any alteration in the colour of delicate pigments, as sometimes occurs when grinding rollers become hot.

The mill shown in the figure is capable of a daily output of 170 lbs. of letterpress ink or 70 lbs. of litho ink, and is driven by an engine of 0.8 horse-power. Larger mills

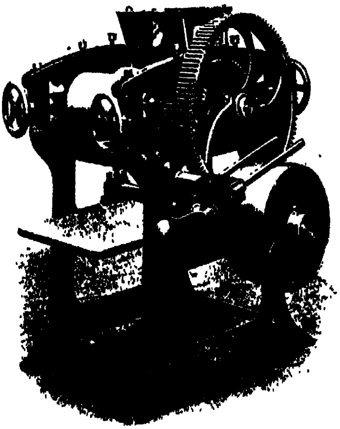

Fig. 38.—Lehmann's Grinding Mill.

constructed by the same firm require 2.5 horse-power, and yield a daily output of 4 cwt. of letterpress ink or 130 lbs. of litho ink, whilst still larger machines have six and nine rollers, and give twice and three times the output.

Combined mixing machines (Fig. 37) and grinding machines are also employed by ink manufacturers.

In *Neal's* grinding mill (Eng. Pat., No. 2640, 1860) the bottom roller alone revolves, whilst the top one is fixed.

A grinding mill patented by *Jackson* (Eng. Pat., No. 957, 1870) contains flat circular grinding plates which revolve on a vertical spindle. On the surface of these plates are teeth, whose cutting faces are arranged half in one direction and half in the other, so that by reversing the motion from time to time half of the teeth are sharpened, whilst the others are in action. The plates are kept cool by means of air-chambers between the fixed and revolving discs.

In a machine protected by *Kingdon* (Eng. Pat., No. 3598, 1873) the rollers were made to revolve in opposite directions, and the upper roller was much smaller than the lower. This arrangement was intended to accelerate the passage of the ink and prevent the darkening that sometimes occurs in grinding coloured inks.

Lithographic Ink.—Printing ink for lithography is supplied in tins, the price ranging from 2s. to 40s. per lb. A fair quality of black ink can be obtained for about 5s. per lb., and it does not deteriorate by keeping. It is in the form of a solid of the consistency of cold wax, and must be thinned down with varnish before it can be used for printing. A small quantity of ink is treated at a time, the varnish being added to it in minute quantities and rubbed down with the palette-knife. The ink is at first difficult to mix with the varnish, but when a little has been incorporated with it it will readily absorb more. A good deal of practice is necessary before the lithographic printer can master the initial difficulties of reducing the ink to a printable condition. He must be guided to a great extent in dilution of the ink by the state of the atmosphere and the temperature.

The lithographer in a small way of business is frequently called upon to print such small things as concert programmes and the like in fancy colours, and must know how to compound inks of different hues. By the aid of a stone, muller, palette-knife, and varnish he should find no difficulty in accomplishing the work. The pigment or pigments employed are rubbed down in small quantities with the palette-knife and with medium or thin varnish, or with a mixture of the two, according to the state of the thermometer. He then grinds the mixture with the muller, gathering it up again with the knife and regrinding again and again. More colour is added as the operation proceeds, and as the ink gradually gains in thickness it will become necessary to do this by scattering the pigment over the stone, and grinding down with the muller without the intervention of the palette-knife. But the latter must be employed to scrape the colour from the stone, pile it up before submitting it again to the action of the muller. Ink thus prepared works better if kept for a day or two before being used.

For delicate tints, as in painting with opaque pigments, it is necessary to incorporate with the colour a considerable body of white, and for this purpose there is nothing better than zinc oxide. It is true that white-lead has more covering power, but there is considerable risk of chemical change occurring when it is mixed with certain other pigments. A transparent alumina introduced by Messrs. *Middleton and Co.* affords an excellent means (in conjunction with oil) of rendering a coloured ink paler without changing its consistency. In chromolithography an ink is sometimes employed for a pale tint, or for enriching a colour already printed, in the same way that a water-colour is used by a painter; that is to say, the ink is sufficiently thinned down by varnish to make the paper show through it. This device has the advantage of reducing the number of separate printings and so saving expense. It is not applicable to printing from type. It is almost unnecessary to state that in printing establishments where a large amount of colour work is done, the inks are ground in mills, or are supplied ready compounded.

Collotype Ink.—The usual practice of the collotypist is to rub down lithographic chalk ink with "middle" varnish, turpentine, and olive oil, and when he requires inks of different colours, he mixes each severally with a little turpentine before incorporation with the other media. It is also customary to add to black inks a small proportion of Prussian blue, indigo, or Venetian red to improve the tone. A special inking slab and muller are used for each colour.

Schnauss * gives definite directions for preparing ink for collotype work on these lines. From our own experiments we can affirm that much depends in the collotype process upon the thorough incorporation of the ingredients of the ink, upon its even distribution, and upon the degree of moisture in the atmosphere, which has an influence upon the gelatine surface.

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* *Collotype*, p. 56

CHAPTER XI.

COLOURED PRINTING INKS.

CONTENTS.—Early methods—Manufactured inks—Painters' pigments—Early ignorance as to proper pigments—Half-tone process block—Necessity of cleanliness—Overlays—Coarse grain screens—Theory of colour—Diagrams of colour—Peculiarities of pigments—Permanency of pigments—Yellow pigments—Red pigments—Blue pigments—Green pigments—Purple and orange pigments—Brown pigments—"Art" shades. **Three-colour printing**—Photographic falsification of colour—Coloured screens—Clerk-Maxwell's work—Colour screens or filters—Coloured light—Pure pigments unknown—General considerations—Examination of trichromatic prints—The half-tone dot—Necessity for transparent inks—Opacity of yellow pigments—Supplementary key block. **Inks for cheques and bank notes**—Patent inks for cheques.

Early Methods.—Interesting details as to the use of coloured inks in printing in the early part of the last century may be gleaned from the large volume by *Savage*.* This contains many illustrations in colour, with a specimen block of each pigment employed. The latter are useful as witnesses of permanency, but the fact must be taken into consideration that these specimen tints have not been exposed to the action of light. Among the colours illustrated we find bistre, sepia, smalt, cobalt and some others which are now seldom employed by the ink manufacturer.

It is worthy of notice that *Savage* makes no allusion to the purchase of coloured inks, and we may presume therefore that up to the date of this book, and possibly for some time afterwards, printers were dependent for these upon their own resources.

Manufactured Inks.—A later author, *Ringwalt*,† remarks that "in the present advanced state of ink-making" it is better for printers to rely upon the manufactured article than to attempt to make their own inks. And he suggests that the difficulty of reducing these inks and mixing them with varnish in the best way to meet the necessities of the work in hand, is quite enough in itself, without the trouble of compounding the inks being added to it. If, however, the printer should insist on being independent in this matter he is referred to *Houghton's* book * for further information on the subject of ink-making.

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* *Practical Hints on Decorative Printing*, 1822.

† *The American Encyclopedia of Printing*. Philadelphia, 1871.

Referring to *Houghton*, we find that he admits that coloured inks can be purchased ready for use, but complains that they are dear, and that the required tints cannot always be readily obtained. He advises the printer therefore to buy his own raw materials and to mix them for himself—taking care that the colours employed are of the best. The appliances and materials necessary consist of a muller, a marble slab and palette-knife, a can of printer's varnish and the raw colours. He then gives a review of the best colours to use.

Paintors' Pigments.—We may take it as a general rule that pigments used by painters can, with very few exceptions, be adapted to the printing-press, always remembering that the painter is not limited to a certain thickness of material. He can if he likes, and as many do, pile on the paint with a palette-knife so that it lies on the canvas in prominent ridges. The printer, on the other hand, must use his colours in such thin layers that their thickness cannot be measured even by a micrometer. It is obvious that this means that the pigment used must have great body or covering power, unless it is intended by printing one colour above another to get a compound tint.

Early Ignorance as to Proper Pigments.—In a smaller book by *Savage* of later date † a chapter is devoted to coloured inks, in which he deplores the ignorance of printers and ink-makers concerning colours and their application to the press. He advises the use of slab and muller, and good printing ink varnish, and in cases where the ink shows a tendency to accumulate upon the type recommends the addition of curd soap—which must be rubbed into the ink with the muller. He then repeats in slightly amplified form the particulars of the different pigments which he gives in his previous work. It is interesting to note that he advocates the use of carmine for a crimson ink, but only for very particular purposes, adding naively, "I have been accustomed to pay for the best two guineas an ounce."

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* *Printer's Everyday Book*, 1856.

† *On the Preparation of Printing Ink both Black and Coloured*, 1832.

The Half-Tone Process Block.—The introduction of the half-tone photographic process block, which has largely superseded the art of wood engraving, caused quite a revolution in printing methods. The etched dots upon these blocks are so fine in character that the work is comparable to a steel engraving rather than to one upon wood; and if one cares to look up the files of any illustrated journal of the period when these blocks first came into use, he will see what deplorable things the printers made of them. Neither the paper nor the ink were good enough to meet the needs of these finely etched blocks; and although we must regret the decline of the beautiful art of wood-engraving, we must put to the credit of the process block a revivification of the printer's art which has been beneficial from every point of view.

Necessity for Cleanliness.—Printers are beginning to see that under the new conditions cleanliness, as well as care, is needed at every stage of the work. When type and electros from comparatively coarse wood-cuts, both of which were treated with black ink only, were the sole requisites of the printer's art, the workshop was the home of grime, perhaps necessarily so. But now that the work entails the employment of delicately etched process blocks much greater care is needed. The place must not only be kept scrupulously clean, but a uniform temperature must be maintained if good work is to be produced. The common use of the electric motor for driving the machinery has banished most of the dirt; and the question of temperature is not a difficult one to solve. The black ink used for process blocks must be of the finest description, and it is found in practice that they take up far less ink than either type or woodcuts. The layer of ink is so very thin that it is a matter of necessity that it should have good covering power, otherwise the impression will appear to be grey and flat.

Overlays.—These blocks require to have the pressure so adjusted that it is greatest in the shadows, less in the half-tones, and lightest of all in the high lights. This desideratum is secured by overlays, and a great improvement has been effected by the recent introduction of an overlay made of guttapercha on paper, which is produced by a photographic process. This overlay, which is specially adapted to the process block, has been introduced from America and is known by a patent name.

Coarse-Grain Screens.—In the case of rapidly printed newspapers on rotary machines, half-tone blocks made with coarse-grain screens are coming more into use every day and displacing the line-drawing—it is often found advisable to use a finer grade of ink for the pages bearing the illustrations than for those containing the text. In higher class journals the custom has recently obtained of printing fine-grain half-tone blocks in coloured ink while the accompanying text is in black. This of course involves separate printing unless a two-colour machine is employed. The effect of the two colours on one page is often most artistic.

Theory of Colour.—It would be beyond the scope of this work to devote much space to the theory of colour, although we are fully alive to the undoubted advantages to be secured by all those having to deal with colour, by an understanding of the principles upon which that theory is based. There are so many excellent manuals upon the theory of colour, the harmony of colours, and upon the use of pigments generally, that all who desire to acquire knowledge upon these subjects will have no difficulty in finding instructors.

Diagrams of Colour.—Many diagrams have been published for showing at a glance the so-called primary colours, and their relation to the secondary and tertiary tints, but the most simple is a very old one which we here reproduce (Fig. 39), and in doing so we must express our regret that we cannot discover the name of its originator. It is extremely useful in at once fixing upon the mind the nature of colour relation so far as pigments are concerned.

The central disc is black, which represents a mixture of the three primary colours—surrounding the disc we find the primaries, yellow, red, and blue. In the next concentric ring are the three secondaries, made up of mixtures of the two primary colours which lie against them. Thus

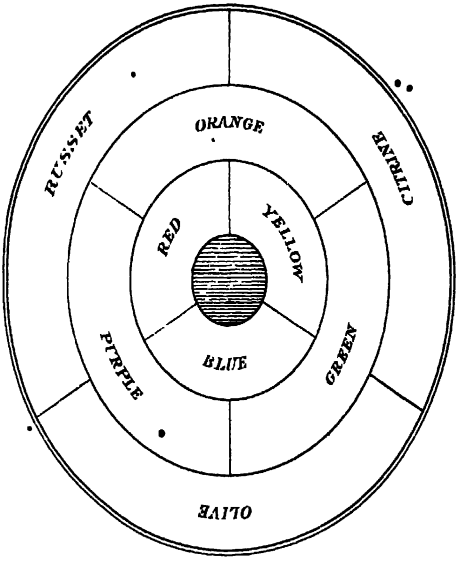

Fig. 39.—Colour diagram.

orange is a mixture of red and yellow, green of yellow and blue, and purple of red and blue. Here too we have a ready guide to the complementary colours, a mixture of any two of the primaries, constituting the complementary tint to the remaining primary. Thus green, made up of blue and yellow, is complementary to red; orange to blue and purple to yellow.

In the outermost ring are the tertiary tints made up of mixtures of the secondaries, thus—green and orange form *citrine*; orange and purple, *russet*; green and purple, *olive*.

Peculiarities of Pigments.—The worker who has hitherto confined his attention to black printing will find upon dealing with colours that he has difficulties to meet which at first may seem to be insuperable. Each coloured ink appears to have its own peculiarities, and where, with a black ink, it is possible to temper it with various media so as to alter its working qualities, coloured ink cannot in many cases be so tampered with. A colour can of course be modified by the addition of white to lighten it, or black to darken it; but what we mean is, that where delicate coloration is necessary, the wholesale addition of turpentine, oil, varnish, &c., is not permissible. Inks of various colours are now purchasable which need no such additions.

Permanency of Pigments.- Up to recent times the colours employed in the manufacture of printing inks were with a few exceptions of mineral origin, and such colours are as a general rule permanent in their nature. And permanency is one of the principal considerations in the selection of a colour, unless the work that the ink is intended for be of quite an ephemeral character.

Aniline Colours.—When the aniline colours first became available in the arts, printers, like many others, were attracted by the gorgeous tints presented by them. The new dyes were quickly made into inks, and bizarre posters with colour schemes never before dreamt of even by those afflicted with acute chromatic aberration appeared on the street hoardings. But only for a brief time, for sunlight mercifully bleached out several of the colours before the prints were many hours old. Any one can test for himself the fugitive nature of most of these aniline colours by exposing any surface coloured with one of them under a negative in an ordinary photographic printing frame.

It is the belief of many workers that this charge of instability which is brought with such good reason against the aniline colours will some day be removed, and that in course of time aniline colours will be produced to which no exception can be taken on this score. We shall see, when we come to consider the requirements of the three-colour system of printing, that such colours are greatly in demand.

The experiments of Prof. *Church* * on the stability of different oil paints exposed to the action of light and air under similar conditions for periods of two or five years are very instructive, and supplement the experiments of Sir *William Abney* and Dr. *Russell* on moist water colours (p. 114).

The following were some of the most important results obtained, the depth of the initial colour in each case being represented by 10:

Naples yellow	10.0	No change
Madder red .	10.0	"
Madder carmine	9.5	"
Madder brown	9.0	"
Artificial ultramarine	10.0	"
Prussian blue . .	8.5	slightly greener.
Indigo .	8.0	" "
Indian yellow	8.0	slightly brown
Yellow ochre .	10.0	browner.
Crimson lake	1.0	almost gone.
Aureolin	9.0	no change.

As coloured printing inks are essentially a kind of oil paint, it is not unjustifiable to assume that closely similar results would have been obtained with the same pigments incorporated with lithographic varnish.

Fugitive Colours.—Want of permanence is thus a fault which is to be attributed to other colours besides those derived from aniline; and those who would seek information upon this point cannot do better than consult Professor *Church's* book, where a table is given in which pigments are divided into three groups—Class I., containing the truly permanent colours; Class II., those which are subject to a certain amount of change, but which may be used; and Class III., comprising those which ought to be definitely excluded from use.

Following the order adopted in the table referred to, we will now briefly consider the various pigments which are of interest to the printer and manufacturer of printing inks.

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* *Chemistry of Paints*, p. 346.

White Pigments.—The white pigments named in Professor *Church's* list are three in number, *baryta white*, *zinc white*, and *flake white*. The first named is not used in the making of ink, but it is of secondary interest to the printer in that this description of white is much used in the preparation of surface paper, which is now so much in demand for the effective printing of half-tone process blocks. *Zinc white*, or *zinc oxide*, is much in request by the water-colour artist on account of its permanency; but it is not so satisfactory for printing purposes as *white lead* or *flake white*. All these three pigments appear in Church's list as first-class pigments in the matter of permanency, if used for oil painting. But when the particles of lead carbonate are not wrapped up in oil, *i.e.*, when used for water-colour painting, the pigment is rapidly attacked by any sulphurous contamination in the air, and quickly blackens.

Yellow Pigments.—Of yellow pigments there is a very great variety, and although printing in yellow ink is not by itself often called for, except perhaps in poster work, the admixture of yellow with other colours in the formation of secondary and tertiary tints gives it an importance which it might not otherwise possess. We must remember, too, that in the modern three-colour process yellow is one of the three primary tints upon which that process depends for its efficiency.

The most important of all the yellows to the printer is *lead chromate*, usually known as *chrome yellow*. By mixing the neutral chromate with lead oxide yellows of various tones, including the orange, may be obtained. For lighter chromes, lead sulphate, while a mixture of lead chromate and sulphate is employed in the production of certain tints. Here again we have a series of pigments which, while unstable when employed as water colours, are comparatively safe when locked up in oil or varnish as in the manufacture of inks. Chrome yellow, combined with Prussian blue and with black, gives a great variety of greens. *Vanadium yellow*, *king's yellow* (*orpiment*), *alizarine yellow*, and *alizarine orange* are all liable to change, and the same may be said of *yellow lake*, *brown pink*, *yellow madder*, and *Italian pink*. *Cadmium yellow* and *cadmium orange* may be placed among the permanent colours, but they are too expensive for common use. Of all these yellows, *chrome yellow* is to be preferred on account of its easy working and freedom from grittiness.

Yellow ochre, *Roman ochre*, and other earths are durable pigments, and are of use to the printer when bright yellow tones are not required. They are also useful for admixture with Prussian blue and other pigments for the production of composite colours. *Raw sienna* and *burnt sienna* come under the same category, the first being a yellow and the second a brownish red. These last named pigments are extremely hard and require careful grinding.

Red Pigments.- There are many red pigments which can be used in the preparation of printing inks. *Vermilion*, which is found in the form of *cinnabar* (mercuric sulphide), in many parts of the world, or can be prepared artificially, is tempting because of its beautiful scarlet colour. But ink prepared from it cannot be employed with lead type, for that metal decomposes the mineral and changes its colour. Otherwise there is no reason to suspect the permanency of vermilion when associated with oil or varnish, and Professor *Church* places it among the first-class pigments.

Vermilion, prepared from native cinnabar, was used in the decoration of the walls of Pompeii, wax being the medium with which it was associated. The colour has not faded, although nearly twenty centuries have gone by since the doomed city was overwhelmed by the ashes from Vesuvius. We must, of course, take into consideration that light has been excluded. The Chinese cinnabar is so pure in quality that it merely requires grinding to convert it into the well-known scarlet pigment. Vermilion of first-rate quality is expensive, and cannot come into common use as an ink.

Madder.—One of the most valued reds has always been that derived from the madder plant—*Rubia tinctorum* of Linnaeus—and until comparatively recent times large tracts of land in India, as well as in the Levant, Holland, and France, were devoted to its cultivation, chiefly for dyeing purposes. But owing to the synthetical production of its chief constituents, *alizarine* and *purpurine*, from anthracene, the cultivation of the madder plant may now be regarded as a discarded industry. Anthracene is derived from coal-tar, and the colouring-matters which it affords are apparently identical with those formerly obtained from the madder plant. A great variety of different reds, such as *madder carmine*, *rose madder*, *pink madder*, *brown and purple madder*, are obtained from alizarine and purpurine. The best qualities are fairly permanent, but some of the tints are liable to change their tone. The madders come under Class II. in Professor *Church's* list.

Carmine.—Carmine, a very unstable compound prepared from the cochineal insect, is sometimes employed to give a fictitious brilliancy to dull reds, but it is so much more expensive than alizarine that it does not now often come under the notice of the ink manufacturers.

Iron Oxide.—*Indian Red*, *Turkey Red*, *Persian Red*, seem to be different names for the same thing, ferric oxide, or iron rust. Although not suitable for fine work when used by itself, it is valuable for mixtures with other pigments. Light red and Venetian red are pigments of similar tint, and are varieties of red ochres.

Blue Pigments.—*Ultramarine* is perhaps the most beautiful of the blue pigments, whether it be natural, *i.e.*, made from *lapis lazuli*, or artificial. The artificial ultramarine, one of the cheapest colours, is alone likely to come under the notice of the printer. Ink made from it is unsatisfactory. It will not work well, and the impressions, even under the hand of a skilled man, are uneven and rough in appearance.

Prussian Blue, on the other hand, has many good qualities to recommend it, and it makes a variety of useful tints when mixed with other pigments. It is transparent, and has great tinctorial power, but when much diluted, or made into a light tint by admixture of a white pigment, is seen to have a greenish hue. Ink made from Prussian blue is generally regarded as being permanent, but it is liable to become pale when exposed to alkaline fumes, such as ammonia. For this reason Prussian blue inks should not be employed in the printing of labels for soap or other substances of an alkaline character.

Cobalt is a permanent blue, but is seldom used by the printer; and the same may be said of *indigo*, an unstable colour, but one which, with certain yellows, affords useful greens.

Green Pigments.—Green pigments for use in the printing press are generally compounded of *Prussian blue* and *chrome yellow*, both of which pigments have already been considered. But *chromium oxide*, a remarkably stable compound, is also occasionally used for very fine printing, such as that of bank notes.

Many greens, like *Emerald green*, *Scheele's green*, *Paris green*, &c., are combinations of copper and arsenic, which are highly poisonous. The first-named possesses a tint of great beauty, which cannot be equalled by any combined pigments, but it is such a very bad working colour that it is not made up as a printing ink. It has, however, sometimes been dusted on to a printed varnish in the same way that bronze powder is attached to such varnish; but the practice must be fraught with so much danger to all concerned that only ignorance of the results to be expected could pardon its employment in this way.

Purple and Orange Pigments.—The other secondary colours, orange and purple, are generally compounded from the primaries, and they do not need further description at our hands. An endless variety of different tones is procurable by using the constituent primaries in varied proportions.

Brown Pigments.—Under the head of brown pigments come a number of earths which owe their coloration principally to *iron oxide*, such as, *ochre*, *umber*, *vandyke brown*, &c. These earth colours are permanent, and are useful in compounding the coarser kind of printing inks. But it should be noted that for the printing of delicate half-tone blocks such natural colours are quite unsuitable. They always retain their gritty character, even after the most thorough grinding, and this has a very prejudicial effect upon the blocks, which under such treatment soon exhibit signs of wear and tear.

"**Art Shades.**"—For such work browns of far richer tone and finer substance may be made by mixing alizarine and other reds with black, to which may be added chrome yellow, Prussian blue, and other colours. So-called "art shades" in printing inks, made up of secondary and tertiary colours with a certain admixture of black to sadden the general tone, are now much in vogue. If the component colours be carefully selected, a half-tone block printed in one of these inks, provided that it has plenty of contrast between full shadow and light tint, appears as if produced by two printings. Such inks have been described for this reason as *double-tone inks*.

It may be mentioned here that such colours as *ochre*, *umber*, &c., which are rich in oxygen, do not require the addition of any separate drying medium when used in the manufacture of printing ink.

THREE-COLOUR PRINTING.

Trichromatic Printing.—It is when we come to consider the effect of the introduction of the process block upon colour work that we find changes of the most radical character, not, of course, in the production of mere monochrome impressions, but in the practice of the three-colour, or, as it is often called, the trichromatic method of block printing.

It is not within the scope of this work to consider how far the modern three-colour method of printing will supersede chromo-lithography; probably there will be found an ample field of employment for both processes. But it will be necessary to give a brief outline of the principles upon which this modern method of producing pictures in colour depends. Like the half-tone process block, the three-colour method of printing is born of the art of photography.

Photographic Falsification of Colour. It has long been known that the photographic plate gives a very false rendering of coloured objects, blue and violet being represented as white, while the warmer tints are shown as black. To understand the underlying cause of this falsification it is necessary to refer to Fig. 40, which represents the solar spectrum in triplicate. In the centre it is shown diagrammatically in the usual manner, with the principal Frauenhofer lines marked by initial letters.

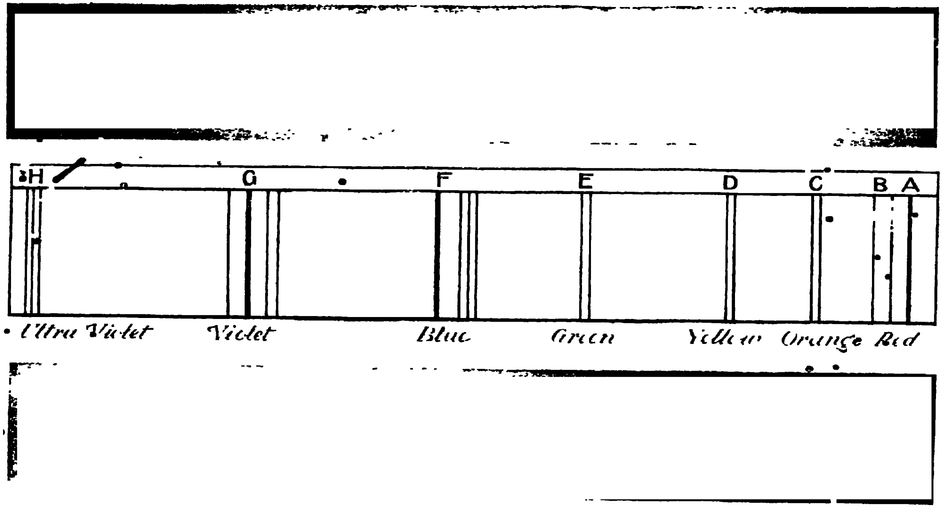

FIG. 40.—SOLAR SPECTRUM IN TRIPLICATE

Also indicated in this diagram are the prismatic colours, from violet to red. Above the diagram the graduated strip shows how the spectrum appears to the eye, the greatest intensity of the light culminating in the yellow region, and falling away gradually into the red at one end and into the violet at the other end of the scale.

Below the diagram we see a similar graduated strip, representing the solar spectrum as reproduced on the photographic plate, and we are able to note at once that the place of greatest intensity is not near the yellow region, but is far away at the violet end of the spectrum. This is a graphic manner of explaining why upon the photographic picture blue is represented as white, and green, yellow and red as black, or nearly so.

Isochromatic Plates.—To Professor *Vogel* is due the discovery that, by associating with the gelatine emulsion which constitutes the surface of a photographic plate certain aniline dyes, its sensitiveness to what we generally call the warmer colours of the spectrum is much increased. These plates are known as isochromatic or ortho-chromatic, and are used in the camera in conjunction with a coloured screen. The exact position of this screen is unimportant, but a convenient plan is to mount the lens of the camera upon a kind of false front with a slit behind it in which the screen can be inserted.

Coloured Screens.—A simple yellow screen or filter consisting of a glass trough holding coloured liquid, or more conveniently a glass plate coated with coloured gelatine, will, in conjunction with an isochromatic plate, be of service in ordinary landscape work. For example, the brilliant yellow blossoms of gorse in the springtime would be represented as black by an ordinary plate, but with the isochromatic plate and screen they would be almost white. The foliage tints of autumn can also be now rendered in a manner far more true to nature than was possible before Professor *Vogel's* discovery.

Photography and Coloured Objects.—But when we come to the representation by photography of oil and water-colour pictures, and different works of art in which colour is an important feature, far more care is necessary in the selection of a proper light filter. The word filter is used advisedly, for the function of the screen is to prevent certain rays passing it, while it gives passage to others. In other words, the required colour is filtered from its associated tints.

Clerk-Maxwell's Work.—The pioneer in this work was Professor *Clerk-Maxwell*, who as long ago as the year 1861 showed in an imperfect manner, for the isochromatic plate had not yet been conceived, that three pictures photographed from one coloured original, but each under a differently coloured screen or filter, would, when combined under suitable coloured lights, amalgamate into a fair representation of the object photographed. *Maxwell's* colour curves have formed the basis of all work in this direction since his time. A representation of these curves is given at Fig. 41. We here see the proportion of the spectrum of which each of the three-colour filters should consist, the red taking in a certain part of the yellow and green, the green overlapping the red and blue, while the blue comprises the violet and part of the green.

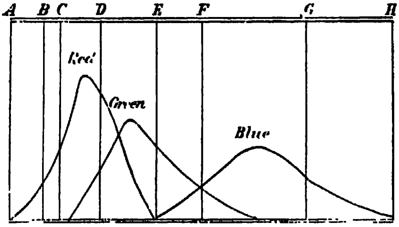

Fig. 41.—Clerk-Maxwell's colour curves.

Colour Screens or Filters.—By mixtures of certain aniline dyes, and staining with them glass plates coated with gelatine, screens or light filters can be made to closely approximate in tint to Maxwell's curves. In photographing a coloured object, say an oil painting, three negatives are made, each under its respective colour filter. From these negatives half-tone blocks are prepared, and it is the printer's business to superpose the images from those blocks in three coloured impressions so as to give a fair representation of the original coloured object.

Coloured Light.—In dealing with coloured light we find that if we mingle upon a screen the colours red, green and blue, from three lanterns we produce white, or an approach thereto, for white light is composed of all the colours of the spectrum. But if we mix together pigments of the same tones we produce black. In the one case we are working with coloured lights, and in the other with coloured shadows. And when we come to handle pigments such as are employed by painters, and in the manufacture of printing ink, we must regard as primary or foundation colours, blue, red, and yellow.

Pure Pigments unknown.—There is unfortunately no such thing as an absolutely pure pigment, and we can never hope really to match the rainbow colours of the prism, otherwise it would be possible to follow with some accuracy the guide afforded by Maxwell's curves. The ideal pigments for printing in three colours have yet to be found; and ink makers are so alive to the importance of the subject that they are devoting much attention to the production of inks which shall, as far as possible, come up to the scientific standard.

General Considerations.—The difficulty with which printers have hitherto had to deal is that the ink makers have not worked hand in hand with the makers of light filters to reach one common goal. The colours of screens and of the inks to be associated with them should be fixed and unalterable. Many workers have been in favour of producing the three inks in the first place, taking care that the pigments are as pure in tone as it is possible to procure them, and then of adapting the colour screens or filters to the pigments so chosen. At present there seems to be much confusion reigning, owing to so many workers acting independently of one another; and it thus comes about that A.'s blocks will give results with inks made by C., which are not possible if B.'s inks are used. That this confusion is quite unnecessary must be apparent when we remember that the exact colours of the inks and screens are based upon scientific principles.

Examination of Trichromatic Prints.—In drawing this chapter to a conclusion, we may note that those who would get a fair idea of the way in which separate process blocks can be made by three printings to give all the varied tints of a polychromatic original object, will learn far more by five minutes' careful examination of a good specimen of three-colour printing than they can from many pages of description.

To examine the print a good magnifying glass is needed, for it is requisite to separate the dots of which the picture is composed, and to note their colour and relation to one another.

The Half-tone Dot.—As in all half-tone blocks, these dots are large and crowded together in the shadows, and comparatively small and widely separated in the lights. In the deepest shadows of all the dots, yellow, red, and blue are superposed one on the other to form a near approach to black. In other places we find two dots of different colours printed above one another, and giving just the same effect as the same two colours mingled on a palette. In other places we find dots of different colours placed in juxtaposition so that the eye mixes them into a compound tint.

Necessity for Transparent Inks.—Now it is obvious that one of the first requisites of the inks used for these built-up tones is that they should possess transparency. An opaque colour, like *vermilion* or *ultramarine*, would at once blot out anything already printed beneath it. We can therefore say at once that such colours are inadmissible for this class of work.

Opacity of Yellow Pigments.—The yellow must be of a sulphur hue, and it is not easy to hit upon exactly the right pigment. A transparent yellow is not at present to be found which is suitable, but the difficulty of opacity is partly overcome by printing the yellow block first. Next in order comes the red, and there is nothing better than the madder lake which is produced from alizarine. We have already seen that its permanency is good, and it is a very transparent colour. For blue we must use Prussian blue, and, as far as possible, the three colours must be so compounded that they possess equal covering power.

Supplementary Key Block.—Some workers have advocated the use of a supplementary key block printed in black or brown in addition to the usual trichromatic blocks. But this can only be necessary when the original screens, or the coloured inks, are at fault, or when the screens do not represent truly the complementaries of the colours used. If the right colours are employed the superposition of the three inks should produce black, and different shades of grey should be possible by varying the proportions of each. The key block is regarded by the foremost workers as a superfluity.

Inks for Cheques and Bank Notes.

Under the head of "Printing inks that change colour on the application of an acid," *Savage*[*] tells us of a black ink, the method of making which was for a long time kept a profound secret "by one house in the city of London," which was designed to prevent fraudulent alterations in bankers' cheques, &c. And he suggests that, in addition to this precaution, the whole paper of such documents should be covered with a delicate lace pattern in a light-coloured ink, so that should any attempt be made to remove writing upon such a draft by means of acid, the pattern and the printed words would disappear as well as the writing ink. The black ink, for which he furnishes a recipe, is made of galls, iron, and logwood, which is precipitated, dried, and ground with soap, turpentine, and balsam of capivi.

For the purpose of printing the lace-like pattern over the surface of the paper he recommends the lake of commerce, ground up with varnish and a large proportion of curd soap. This ink he actually tried, and found that it would not resist oxalic acid, but he states that any colour of vegetable origin might be adapted to the same purpose. He expresses the hope that, from the hints which he has given, the subject will be pursued and the method made perfect,—and asserts that if he should thus prove to be the means of preventing the commission of crime, it would be a source of the highest gratification to him.

[*] *The Preparation of Printing Ink*, 1832.

In the earliest attempts to guard against fraud by alterations in cheques, &c., attention was directed to the writing ink to be used, and numerous so-called "safety inks" (p. 207) were devised. Obviously, however, such inks would only be used to a limited extent, and the necessity for them has been largely obviated by the introduction of various methods of printing the groundwork of the cheque with special inks that would permanently change colour on the addition of any of the usual reagents employed to remove ordinary iron gall inks.

Patent Inks for Cheques, &c.—A process patented by *Scroggan* (Eng. Pat., No. 1744; 1857) was devised to prevent the counterfeiting of bankers' drafts and other documents by photography. Two or more colours were used, each of which "absorbed light." The groundwork of the note was printed in one of these (*e.g.*, yellow, red or orange), whilst the other was made into an ink for printing the design and figures on the note, and was as fugitive as the ground colour. An ink of this type consisted of iron hydroxide and gallic acid ground in boiled linseed oil. Documents thus printed gave only a blurred photographic copy, whilst any attempts to remove the ground colour simultaneously removed the design. *Vogel's* discovery of colour sensitive plates destroys whatever value there was in this invention.

In *Moss's* patent (Eng. Pat., No. 348; 1859) the paper pulp for the notes was incorporated with a pigment, such as chromium oxide or burnt clay; whilst an ink for printing the notes contained burnt China or other clay and sulphur, with or without a pigment. It was stated that any attempt to remove the colour or printing would render the note useless for circulation.

A permanent printing ink for bank notes invented by *Edson* (Eng. Pat., No. 3204; 1863) consisted of a compound of stannic oxide with chromium oxide or other metallic oxide.

In 1876 *Pinkney* (Eng. Pat., No. 4470) claimed a process of treating the note with a substance that would form an insoluble compound with ordinary writing ink, and mentioned in particular soluble non-deliquescent ferro-

and ferri-cyanides with an aniline or vegetable colour as suitable for the purpose.

In *Nesbit's* patent (No. 4204; 1879) ordinary lithographic ink was dried, powdered, and mixed with an aniline dye-stuff soluble in water, the whole being mixed with turpentine or other liquid which would not dissolve the aniline dye-stuff. Cheques printed with this ink would be smeared on applying any aqueous reagent to remove writing.

A special method of preparing paper for cheques by immersion in copper sulphate and ammonium carbonate solution, and subsequently in an alkaline solution of cochineal with alum and glycerin, was provisionally protected by *Haddan* (Eng. Pat., No. 4997; 1879). This paper would change colour on contact with the reagents used to remove writing ink.

A process with the same end in view was patented by *Dupré and Hehner* (Eng. Pat., No. 375; 1881). The preparation used for printing the note consisted of a sulphide insoluble in water, but acted on by dilute acids (*e.g.*, zinc sulphide), with lead carbonate or other salt of a heavy metal. The mixture was worked into a paste with glycerin, treacle, and gum arabic, and could be used for printing invisible characters on the cheque, or added to the coloured paste for printing the groundwork. On applying acid, alkali, or cyanide to a cheque thus treated, dark stains would be produced immediately.

A method of preventing the obliteration of printing ink by means of solvents for oils, and especially the cancelling marks on postage stamps, was devised by *Nesbit* (Eng. Pat. No. 949; 1883). It consisted of the use of a printing ink prepared by incorporating an extract of alkanet root with oil. Any attempts to remove ordinary printing ink would blur the printing done with this ink. In 1896 *Webb* (Eng. Pat., No. 26,992) patented an aniline safety ink for copper and steel-plate printing of cheques and the like.